



AGRICULTURAL RESEARCH INSTITUTE
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and sulfur-free" acid chlorides by the action of silicon tetrachloride on the corresponding organic acid.

DIVISION OF CHEMICAL ENGINEERING,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN.

NOTES

Action of Ethylene on Pure Starch.—It has been found that fruits and vegetables treated with ethylene have a higher sugar content than the same kind of fruits and vegetables not treated with the gas.¹

Because ripening is known to be accompanied by change of starch into sugar the attempt to change pure starch into sugar by the use of ethylene was made.

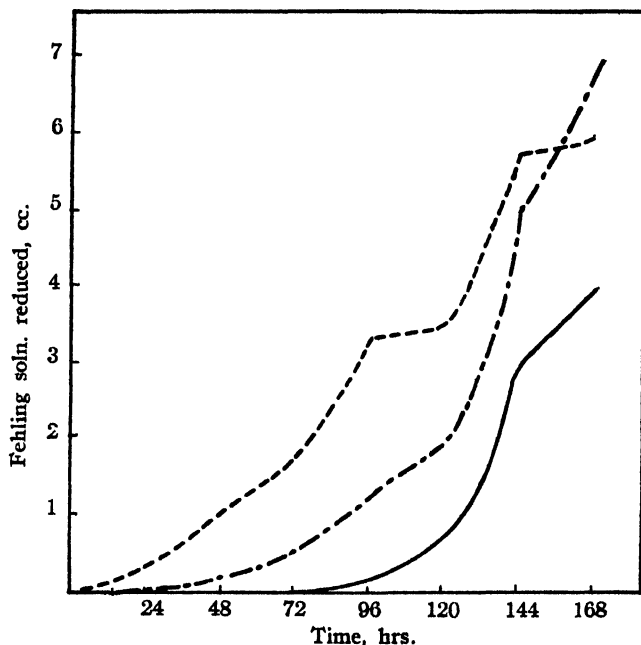


Fig. 1. ----, 10-min. boil; - · - · -, 5-min. boil; — 1-min. boil.

Dry starch (both corn and wheat starch were used) was placed in an atmosphere of ethylene at 21° and atmospheric pressure and, as shown by the Fehling test, was partially changed into a reducing sugar. The action was slow and was accompanied by a change in color from pure white to a pale, yellowish tint. No quantitative determination of the rate of conversion of dry starch was made, merely a qualitative test. Untreated starch showed no change in the same length of time. The same kind of

¹ Harvey and Regeimbal, "Physiology of Blanching Celery," *Proc. Am. Assoc. Advancement Sci.*, Washington Meeting, vol. 79, 1924.

starch, when made into an emulsion with water, was converted into sugar much more rapidly. A similar starch emulsion free from ethylene showed only a minute change even upon long boiling or upon standing for several weeks. The temperature varied from 21 to 24°. Water saturated with ethylene did not reduce Fehling solution. The starch emulsion absorbed about as much of the gas as did pure water, and no further absorption took place when the emulsion was allowed to stand, although the percentage of reducing sugar increased steadily.

Three starch emulsions of different "boiling times" but of the same concentration (1 g. of starch in 100 cc. of water) were saturated with ethylene at approximately 22° and allowed to stand. The first had been boiled one minute, the second five and the third ten minutes and all were allowed to cool to room temperature before they were saturated with the gas. The temperature varied between 20 and 24° while the emulsions were standing.

The rate of conversion of the starch to sugar was found to be affected by the time of boiling; for example, the ten-minute boil was changed more rapidly than the one-minute. The rate was slow at the beginning of the action, but such was to be expected. This "period of incubation" is especially noticeable in the data for the one-minute boil.

TABLE I
CONVERSION OF STARCH TO SUGAR

Time, hrs.	24	48	72	Fehling soln., cc.	96	120	144	168
No. 1	0.0	0.0	0.0	0.1	0.4	3.0	4.0	
No. 5	.0	.2	.5	1.2	1.9	5.0	7.0	
No. 10	.3	1.0	1.8	3.3	3.5	5.8	6.0	

No. 1 boiled one minute, No. 5 boiled five minutes, No. 10 boiled ten minutes, before saturation with ethylene. In each case a 10cc. sample of the well-stirred emulsion was used for the titration. No. 5 showed 57% of reducing sugar at the end of 168 hours, when these observations were discontinued.

The presence of the plateaus in the curve for the ten-minute boil has not been explained at the present time.

It seems demonstrated that an enzyme need not be present, as has been thought, for the conversion of starch into sugar by the action of ethylene. The presence of ethylene alone seems sufficient. The chemistry of the reactions is not known, but it is thought that the gas acts as a catalytic agent, since no absorption was noticed even upon long standing.

This work will be continued at higher temperatures and pressures.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY,
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ROCKFORD, ILLINOIS

HELEN E. REA
R. D. MULLINIX

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The Boiling Point of Para-Cresol.¹—In my article on *p*-cresol,² the literature citations omitted a determination by Clemmensen³ which has just been found in his article entitled "Über eine allgemeine Methode zur Reduktion der Carbonylgruppe in Aldehyden und Ketonen zur Methylengruppe."

He describes (p. 61) the preparation of *p*-cresol from *p*-hydroxybenzaldehyde but makes no statement concerning the source of the *p*-hydroxybenzaldehyde or its purity. The product, after several distillations, finally boiled at the constant temperature of 201°, at 750 mm. pressure.

From these meager data I have calculated the boiling point at 760 mm. pressure by means of Equations 1 and 2 of my previous article. The values found are (1) 201.50° and (2) 201.54°. They afford no basis for modifying my views previously expressed and the boiling point of 202.32° given in my paper.

The object of this note is to complete the literature citations since Clemmensen's determination is one that might be indefinitely overlooked because of the title of his article.

CONTRIBUTION FROM
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H. D. GIBBS

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High Vacuum Distillation.—Sufficient glass wool is placed in the distilling flask to extend slightly above the surface of the liquid. The vacuum distillation of very heavy sirups may be carried out in this way smoothly and without bumping.

CONTRIBUTION FROM THE
DEPARTMENT OF BIOLOGICAL CHEMISTRY,
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ST. LOUIS, MISSOURI

EDWARD S. WEST

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New Fermentation Tube.—In the determination of the qualities of different micro-organisms it is of fundamental significance to know whether the micro-organism is capable of growing in oxygen-containing, oxygen-free or other atmospheres.¹ Up to the present, different bothersome processes have been in use for this purpose. It was found that it is possible to avoid

¹ Published by permission of the Surgeon General, United States Public Health Service.

² Gibbs, *THIS JOURNAL*, **49**, 839 (1927).

³ Clemmensen, *Ber.*, **47**, 51 (1914).

¹ Nord, *Protoplasma*, **2**, No. 2 (1927).

these difficulties in a simple manner through an appropriate reconstruction of the saccharimeter of Einhorn.

When one found it necessary to grow micro-organisms on a suitable nutrition medium in a nitrogen-containing or other atmosphere, it was not possible to carry out this investigation in the present form of the saccharimeter because it does not allow the passing through of another gas. If, therefore, we add a stopcock (Fig. 1) to the longer arm of this tube, it will be possible, by simultaneously inserting a single-holed rubber stopper in the shorter end of the tube, to pass through the nutrition medium and, if necessary, to keep in the space above it whatever gas is wanted. The open surface of the liquid has to be covered simultaneously with liquid paraffin. In the case of nitrogen, the purification of this gas by passage through an alkaline pyrogallol solution is not satisfactory enough for biological purposes. Such nitrogen still oxidizes reduced methylene blue and therefore it is necessary for this purpose to pass it over hot (dark, gleaming) copper spirals.

A fermentation tube constructed in this way can of course also be used as a common saccharimeter; with such a tube, a fermentation may be carried on during which the expected quantity of carbon dioxide produced exceeds several times the capacity of the long arm of the tube. A repeated simple opening of the stopcock renders this possible. It also enables one to investigate the capacity of micro-organisms for nitrogen fixation.

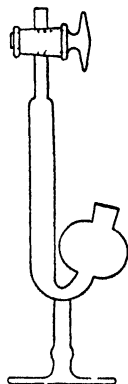


Fig. 1.

CONTRIBUTION FROM THE
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F. F. NORD AND
MOLLIE G. WHITE

NEW BOOKS

Magnetism and Atomic Structure. By EDMUND C. STONER, Ph.D., Lecturer in Physics at the University of Leeds. E. P. Dutton and Company, 681 Fifth Avenue, New York City, 1926. xiii + 371 pp. 56 figs. 22.5 × 14.5 cm. Price \$5.00.

According to the author's statement, this book is to be regarded as a supplement to ordinary works on magnetism, rather than a comprehensive treatise. The general method adopted is "to give tolerably complete outlines of representative researches, and to base discussions on these. Prominence is given to work which is thought to be of most importance and lasting value, but the selection involved is necessarily arbitrary." This mode of treatment makes possible the logical discussion in a book of moderate size of those phenomena of magnetism which bear most directly upon the problems of atomic structure. A more

coherent and readable presentation of the material is thus secured than was attainable in the more comprehensive Bulletin of the National Research Council on "Theories of Magnetism" by several collaborators. Moreover, since the publication of this report, much has been done to advance our knowledge, notably, the fundamental experimental investigations of Gerlach and Stern, and the further development of the Bohr theory of atomic structure. The significance of much of the older material is now apparent in the light of the new, but one is impressed by the fact that, in spite of the vast amount of work that has been done in the field of magnetism, only a beginning has been made in the disentanglement and explanation of the complex phenomena involved. The necessarily mathematical treatment of the material may make many of the details difficult of comprehension to some readers but will not prevent their appreciation of the general significance of the relations. The correlation of information, the indication of problems for research, and the literature references should be valuable to the investigator. The author is to be congratulated on the production of a book suggestive to the specialist and informative to the general reader.

CHARLES P. SMYTH

Handbuch der Anorganischen Chemie. (Handbook of Inorganic Chemistry.) By Dr. R. ABEGG. Vol IV, first part, first half. Oxygen, Sulfur, Selenium, Tellurium and Polonium. By Dr FR AUERBACH and Dr. I. KOPPEL. S. Hirzel, Königstrasse 2, Leipzig, 1927. xii + 966 pp. 61 figs. 17 X 24 cm. Price, unbound, M. 60; bound, M. 64.

The appearance of this already long overdue instalment of the "Handbook" was still further delayed by the death of its editor and chief author, in 1925. At that time about five-sixths of the volume was in type. The task of completing it has evidently been performed with energy and dispatch by I. Koppel, its present editor.

This volume, dealing with elements of such capital importance as oxygen and sulfur, is particularly welcome, not only because it fills a serious gap in the present Handbook, but because these elements and the others of this group have not yet been reached in the new edition of the Gmelin "Handbook" or, with the exception of oxygen, in Mellor's "Treatise." It appears to adhere to the excellent traditions and high standards of the earlier volumes. It does not aim merely to collect every relevant statement in the literature, but rather to present a critical, connected and logical survey of the chemistry of these elements, illuminated by the application of the principles of theoretical and physical chemistry.

ARTHUR B. LAMB

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Die seltenen Erden vom Standpunkte des Atombaus. (The Rare Earths from the Point of View of Atomic Structure.) By Dr. GEORG V. HEVESY. *Struktur der Materie in Einzeldarstellungen.* V. Julius Springer, Berlin, 1927. viii + 140 pp. 15 figs. 22 × 14.5 cm. Price, unbound, Reichsmark 9; bound, Reichsmark 10.20.

This fifth of the new German monographs on the structure of matter is a worthy successor of the excellent works with which the series began. The earlier books make their appeal more exclusively to physicists and to those chemists who follow the bewildering complexities of modern spectroscopy and quantum mechanics, but the present booklet should find a wider circle of chemical readers.

The first part deals with the (Bohr) theory of the constitution of the rare-earth atoms, and the placing of the elements in the periodic table. A rapid survey of the chemical properties and the molecular volumes of the various types of compounds gives many opportunities to relate known regularities to the general features of the Bohr model. The theory is then further elaborated in line with the work of Stoner, Hund, etc., and the absorption spectra and paramagnetism of the ions are discussed in relation to the newer views.

In the second part of the book the more detailed chemistry of the elements is surveyed, including all methods of analytical determination, and the separation processes. The ionic sizes in the sense of Grimm and of Bragg, the geochemistry and the relative abundance of the elements are the next subjects treated, and the book closes with a short historical chapter.

Professor von Hevesy has made a real contribution to systematic chemistry in showing how beautifully the facts of spectroscopy and magnetism, x-rays and densities are related to the more "purely chemical" characteristics of the elements, such as relative base strengths, crystalline form, valence, etc., as soon as both types of regularities are interpreted in terms of the Bohr theory.

Professor Bohr is reported to have remarked that had there been no rare-earth group beginning with lanthanum and ceasing with cassiopeium, his theory must have been abandoned, and certainly in this group we have at once a searching test and a brilliant triumph of the qualitative aspects of that theory.

In these days of Heisenberg and Schrödinger, it is not very clear just how such intimate prying into the atom's internal affairs as the following may need to be rephrased (p. 33). "Now the 4₄ electrons move within the region where the 5₁ and 5₂ electrons are moving throughout the greater part of their paths, with the result that the added 4₄ electron is able to compensate very considerably for the effect of the simultaneous increase of one unit in the nuclear charge."

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Compactly and interestingly written, von Hevesy's book is the best short account of rare-earth chemistry available today, whether one is looking merely for experimental facts or for an attempt at coördination in terms of theory.

NORRIS F. HALL

Radioaktivität. (Radio-activity.) By DR. STEFAN MEYER and DR. EGON SCHWEIDLER. Second, enlarged and partially revised edition. B. G. Teubner, Leipzig, 1927. x + 721 pp. 108 figs. 23.5 × 16.5 cm. Price, bound, RM 36.

In the introduction, the authors defend the subject of radio-activity against the charge of having reached quasi-completeness in 1916, alleging that many really new lines of attack have been laid down in subsequent years. Quantization of nuclear processes, artificial decomposition (and perhaps upbuilding) of atoms are certainly new, and there have been new radio-active elements discovered, new models proposed and much elaboration of detail.

One learns with a certain melancholy that it has been necessary to cite 6430 references in this edition, as compared with 3080 in the earlier one, and the solid, meaty pages which follow (seven hundred of them) testify that radio-activity is no longer a little corner of a subject tucked away somewhere between chemistry and physics, but a field already assuming ample proportions in its own right.

The successive chapters comprise: Historical Introduction, The Processes of Radio-active Change, The Processes of Radio-active Radiation, The Effects of Radio-active Radiations, Measurements and Methods of Measurement, The Individual Radio-active Substances, Radio-activity in Geophysics and Cosmic Physics, Appendix.

The book is valuable for its many up-to-date tables of constants, the painstaking thoroughness of its documentation, and the wide range of the subjects covered. There seem to be no important omissions. Perhaps the least valuable part is that devoted to atomic-structure theory, which is so briefly and uncertainly treated as to be practically useless. This is, of course, a book indispensable to the specialist—others may find that shorter treatments, several of which have recently appeared in English, are adequate to their needs and more convenient to use.

NORRIS F. HALL

The Evolution and Development of the Quantum Theory. By N. M. BLIGH. With a foreword by Professor MAX PLANCK. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1926. 112 pp. 6 figs. 22 × 14.5 cm. Price \$3.00.

In this small book of about one hundred pages the author attempts an account of the quantum theory from its introduction by Planck up to, but not including, the beginnings of the so-called new quantum theory of Heisenberg, Born, Jordan and Schroedinger.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THEORIES OF UNIMOLECULAR GAS REACTIONS AT LOW PRESSURES

BY OSCAR KNEFLER RICE AND HERMAN C. RAMSPERGER

RECEIVED JANUARY 10, 1927

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Certain recent experiments on the decomposition of propionic aldehyde¹ show an actual falling off at low pressures in the rate of a reaction which is unimolecular at high pressures. It would seem that some kind of collision hypothesis must be used to account for activation in such a case. The old form of the collision hypothesis as developed by Langmuir,² Christiansen and Kramers,³ and Tolman⁴ appears entirely inadequate even in the case just cited.⁵ It seems possible that the explanation may be found in the suggestion, originally made by Lewis and Smith⁶ and somewhat extended since by Christiansen⁷ and by Hinshelwood and Lindemann,⁸ that the internal degrees of freedom may be of some help in causing activation.⁸

This theory may be put in several different forms, not all of which have been considered in this connection. These will be investigated, and equations for the reaction rate at low pressures will be developed, using the methods and results of classical statistical mechanics.

¹ Hinshelwood and Thompson, *Proc. Roy. Soc.*, **113A**, 221 (1926).

² Langmuir, *THIS JOURNAL*, **42**, 2201 (1920).

³ Christiansen and Kramers, *Z. physik. Chem.*, **104**, 151 (1923).

⁴ Tolman, *THIS JOURNAL*, **47**, 1524 (1925).

⁵ Hinshelwood, *Proc. Roy. Soc.*, **113A**, 230 (1926).

⁶ Lewis and Smith, *THIS JOURNAL*, **47**, 1514 (1925).

⁷ Christiansen, *Proc. Cambridge Phil. Soc.*, **23**, 438 (1926).

⁸ Since this paper was submitted, articles by Fowler and Rideal [*Proc. Roy. Soc.*, **113A**, 570 (1927)] and Thomson [*Phil. Mag.*, [7] **3**, 241 (1927)] have been received here, in which these authors have considered the internal degrees of freedom. They were attempting to explain quite a different phenomenon, and many of their assumptions run counter to ours. In so far as their treatments coincide with ours, they are similar also to the earlier work of Hinshelwood and Christiansen.

General Considerations

There seems to be some ambiguity over the definition of heat of activation. We shall define it as the minimum energy that a molecule must possess in order that it may decompose. Only internal energy is included and not translational, since we assume with Lewis and Smith⁹ that a fast-moving molecule is no more likely to decompose than a slowly-moving one. The heat of activation is *not* to be taken as the excess over an average energy, nor as an energy term derived from the temperature coefficient of the reaction by use of the simple Arrhenius equation. In general, it is to be supposed that the energy of activation may be distributed in any manner whatsoever among the various degrees of freedom, exclusive of those concerned with the motion of translation of the molecule as a whole.

With this understanding we may now turn our attention to various possible theories.

Theory I.—The simplest possible hypothesis states that an activated molecule has a certain chance of reacting, independent of the distribution of energy among the degrees of freedom and independent of the amount it has above that necessary for activation. This is the theory which has been considered by Hinshelwood.⁵

Theory II.—It might be necessary for reaction that a *particular* degree of freedom should have a minimum energy, say ϵ_0 , but that it is able to obtain this energy, even between collisions, from other parts of the molecule.¹⁰ We shall assume that if the proper degree of freedom gets this energy, the molecule instantly decomposes. Now if the molecule *as a whole* has an energy of ϵ_0 or greater, enough of this energy *may* get to the proper degree of freedom to cause reaction to occur. A molecule is *activated*, then, if its total energy, exclusive of the translational, is at least ϵ_0 . However, the chance that it will *react* depends on the amount of energy it has in excess of ϵ_0 , for this determines the probability that enough energy will reach the right place.

Other Theories.—There may be various modifications of Theories I and II. (a) It may be that if *any one* of a number of unconnected degrees of freedom gets a certain (unshared) energy, the reaction occurs. (b) Reaction may take place if the energy becomes localized, not in a single degree of freedom, but among a few closely connected degrees of freedom, it being supposed that it makes no difference how it is distributed among this limited number of degrees of freedom. (c) It may be necessary for each of several degrees of freedom simultaneously to attain a minimum energy.

The above are typical, but other cases might readily be imagined. We shall consider chiefly Theories I and II.

⁹ Lewis and Smith, *THIS JOURNAL*, **47**, 1512 (1925).

¹⁰ Thomson (Ref. 8) also makes use of this idea.

It is to be remarked that any of the above will, of course, give a unimolecular reaction at high pressures where there is an equilibrium number of activated molecules, for the rate then depends only on the probability that something will occur within a single activated molecule.

Before we can proceed to the main part of this paper it is necessary to make a general statement concerning the method we propose to use in calculating the rate of activation. As already stated, we shall assume that interchanges of energy between molecules occur only at collisions, and we shall consider only the case in which this is the sole means of activation. Hinshelwood¹¹ shows that the rate of activation may be calculated from the rate of deactivation. This idea we intend to use, but we desire to go a little further than he does. If the pressure is high only a small fraction of the activated molecules react, most of them becoming deactivated by collisions with other molecules. The rate of activation is then obviously practically equal to the rate of deactivation. The latter may be calculated from the number of collisions of activated molecules, assuming deactivation at every collision. Now, when the pressure is low, it is no longer true that the rate of activation is equal to the rate of deactivation, because an appreciable number of the activated molecules react instead of becoming deactivated; however, this does not affect the rate of activation, and we can calculate the rate of deactivation which would exist if there were an equilibrium number of activated molecules present, and set it equal to the rate of activation. If the assumption of deactivation at every collision is not absolutely true, the last sentence does not hold, for then, by the principle of entire equilibrium, part of the source of activated molecules will be other activated molecules, whose numbers are depleted at low pressures. Now, it may be that although most of the activated molecules lose energy on collision, a small number actually gain it. One might even suppose that the entire supply of the more highly activated molecules (their number being exceedingly small) was maintained in this way from other less highly but nevertheless activated molecules. This would make no difference in the case of Theory I because of the smallness of number of the high-energy molecules. In Theory II, however, the high-energy molecules have much more tendency to react and this may more than counterbalance the other factor. It will, therefore, be necessary to make an *a posteriori* calculation to show that our assumption is justified, or to indicate how much it may lack of being true.

We may now proceed, confining ourselves throughout to the situation existing at the beginning of a reaction, where we may consider that we have a pure gas, the reaction products not yet beginning to have an effect.

¹¹ Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926, p. 127.

$$K = \int_{\epsilon_0}^{\infty} K_{\epsilon} d\epsilon = \int_{\epsilon_0}^{\infty} \frac{W_{\epsilon} b_{\epsilon} d\epsilon}{1 + b_{\epsilon} kT/(ap)} \quad (8)$$

where p/kT has been substituted for N . It will be noted that for high pressures b_{ϵ} is negligible compared to aN and we have

$$K_{\infty} = \int_{\epsilon_0}^{\infty} W_{\epsilon} b_{\epsilon} d\epsilon \quad (9)$$

By the general principles of statistical mechanics¹⁶ under the same assumptions as before

$$W_{\epsilon} d\epsilon = -\frac{1}{\left(\frac{n}{2}\right)} \left(\frac{\epsilon}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon}{kT}} \frac{d\epsilon}{kT} \quad (10)$$

We now have to evaluate b_{ϵ} .

Let us consider a number of molecules, all of which have energy between ϵ and $\epsilon + d\epsilon$, ϵ being greater than ϵ_0 . These we shall designate as molecules of Class A. There will then be a certain chance that a molecule of Class A will have an energy larger than ϵ_0 in a particular degree of freedom. We will call such a molecule a molecule of Class B. If a state of equilibrium existed, these molecules would be shifting over at a certain rate (between collisions) to molecules which, while still of Class A, would not be of Class B. Let us suppose that this rate is proportional to the number of Class B, and is independent (1) of the excess of energy in the particular degree of freedom¹⁷ and (2) of ϵ .¹⁸ Now the rate at which molecules of Class B are formed under equilibrium conditions is equal to the rate at which they revert to molecules of Class A and not of Class B, and hence is proportional to the number of Class B. If all molecules of Class B decompose, this does not affect the rate at which they are formed. Hence the rate of decomposition is proportional to the number of Class B which would normally exist in a state of equilibrium.

We have, then, to determine the fraction of all molecules which have total energy between ϵ and $\epsilon + d\epsilon$ and which would also have, if the distribution law held, one degree of freedom with energy greater than ϵ_0 .

The chance that one particular degree of freedom has an energy between ϵ_1 and $\epsilon_1 + d\epsilon_1$ is

¹⁶ Gibbs, "Elementary Principles in Statistical Mechanics," Scribner's, New York, 1902, p. 93.

¹⁷ This certainly cannot be a bad assumption to make for purposes of approximation, for the distribution law shows that the number of molecules having any appreciable excess over ϵ_0 in the particular degree of freedom is very small compared with the number having a slight excess, and hence those with a large excess do not greatly affect the calculation.

¹⁸ The shape of the curves K_{ϵ} against $\epsilon - \epsilon_0$ later to be obtained (Fig. 1) would indicate that this should be satisfactory for purposes of approximation, unless the effect of ϵ is quite marked.

$$\frac{1}{\sqrt{\pi}} \left(\frac{\epsilon_1}{kT} \right)^{-\frac{1}{2}} e^{-\frac{\epsilon_1}{kT}} \frac{d\epsilon_1}{kT} \quad (11)$$

The chance that all the rest of the degrees of freedom have among them an energy between $\epsilon - \epsilon_1 - d\epsilon_1$ and $\epsilon - \epsilon_1 + d\epsilon_1$ is

$$\frac{1}{\Gamma\left(\frac{n-1}{2}\right)} \left(\frac{\epsilon - \epsilon_1}{kT} \right)^{\frac{n-3}{2}} e^{-\frac{\epsilon - \epsilon_1}{kT}} \frac{d\epsilon + d\epsilon_1}{kT} \quad (12)$$

The product of Equations 11 and 12 is evidently greater than the probability that a molecule should have energy between ϵ and $\epsilon + d\epsilon$ and at the same time should have an energy between ϵ_1 and $\epsilon_1 + d\epsilon_1$ in one (specified) degree of freedom.¹⁹ Similarly, if we had written $d\epsilon - d\epsilon_1$, instead of $d\epsilon + d\epsilon_1$ (assuming $d\epsilon_1 < d\epsilon$), then their product would have been smaller. If $d\epsilon_1$ is small compared with $d\epsilon$, then it does not matter which way Equation 12 is written, and we may write it simply

$$\frac{1}{\Gamma\left(\frac{n-1}{2}\right)} \left(\frac{\epsilon - \epsilon_1}{kT} \right)^{\frac{n-3}{2}} e^{-\frac{\epsilon - \epsilon_1}{kT}} \frac{d\epsilon}{kT} \quad (13)$$

It is now evident that the product of Equations 11 and 13 may be integrated with respect to ϵ_1 , holding ϵ and $d\epsilon$ constant. This removes the limitation that $d\epsilon_1$ must be small compared to $d\epsilon$.²⁰

Multiplying Equations 11 and 13 and integrating with respect to ϵ_1 from ϵ_0 to ϵ will give us $\alpha W_{\epsilon} b_{\epsilon}$, where α is a constant, independent of ϵ , which will be determined later.

$$\alpha W_{\epsilon} b_{\epsilon} = \frac{1}{\sqrt{\pi} \Gamma\left(\frac{n-1}{2}\right)} \frac{e^{-\frac{\epsilon}{kT}}}{(kT)^{\frac{n}{2}}} \int_{\epsilon_0}^{\epsilon} \epsilon_1^{-\frac{1}{2}} (\epsilon - \epsilon_1)^{\frac{n-3}{2}} d\epsilon_1 \quad (14)$$

For any definite value of n the integral in this expression could be evaluated by successive integration by parts. We will, however, be content with an approximation. We see that $(\epsilon - \epsilon_1)^{(n-3/2)}$ varies much more rapidly, assuming n to be fairly large, than $\epsilon_1^{-1/2}$, and that the important part of the integrand is the part where ϵ_1 is small. We therefore write as an approximation

$$\int_{\epsilon_0}^{\epsilon} \epsilon_1^{-\frac{1}{2}} (\epsilon - \epsilon_1)^{\frac{n-3}{2}} d\epsilon_1 = \epsilon_0^{-\frac{1}{2}} \int_{\epsilon_0}^{\epsilon} (\epsilon - \epsilon_1)^{\frac{n-3}{2}} d\epsilon_1 = \frac{2\epsilon_0^{-\frac{1}{2}}}{n-1} \frac{(\epsilon - \epsilon_0)^{\frac{n-1}{2}}}{2} \quad (15)$$

¹⁹ This is seen in the following manner. Suppose the one degree of freedom to have an energy exactly ϵ_1 . Then if all the other degrees of freedom together can have an energy between $\epsilon - \epsilon_1 - d\epsilon_1$ and $\epsilon - \epsilon_1 + d\epsilon_1$, the total energy of the molecule can lie anywhere between $\epsilon - d\epsilon_1$ and $\epsilon + d\epsilon_1$. This evidently includes every molecule in which the one degree of freedom has an energy of exactly ϵ_1 and in which the total energy is between ϵ and $\epsilon + d\epsilon$, and some others besides. The same can be seen to be true for any value we choose to take between ϵ_1 and $\epsilon_1 + d\epsilon_1$.

²⁰ For treatment of a similar problem see Lorentz, "Théories Statistiques en Thermodynamique," Teubner, Leipzig and Berlin, 1916, p. 12.

To evaluate α we substitute Equation 15 in 14 and integrate with respect to ϵ from ϵ_0 to ∞ . This gives us

$$\alpha \int_{\epsilon_0}^{\infty} W_{\epsilon} b_{\epsilon} d\epsilon = \frac{2\epsilon_0^{-\frac{1}{2}} e^{-\frac{\epsilon_0}{kT}} (kT)^{\frac{1}{2}} \Gamma\left(\frac{n+1}{2}\right)}{(n-1) \sqrt{\pi} \Gamma\left(\frac{n-1}{2}\right)} \quad (16)$$

Evaluating α from Equations 16 and 9 and inserting the value in Equation 14 we have

$$W_{\epsilon} b_{\epsilon} = \frac{K_{\infty}}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{-\frac{\epsilon-\epsilon_0}{kT}}}{kT} \left(\frac{\epsilon-\epsilon_0}{kT}\right)^{\frac{n-1}{2}} \quad (17)$$

From 17 and 10

$$b_{\epsilon} = \frac{K_{\infty} \Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{\frac{\epsilon_0}{kT}}}{(kT)^{\frac{1}{2}}} \frac{(\epsilon-\epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}} \quad (18)$$

Equation 8 now becomes

$$K = \frac{K_{\infty}}{kT \Gamma\left(\frac{n+1}{2}\right)} \int_0^{\infty} \frac{e^{-\frac{\epsilon-\epsilon_0}{kT}} \left(\frac{\epsilon-\epsilon_0}{kT}\right)^{\frac{n-1}{2}}}{1 + \frac{\beta_2}{p} \frac{(\epsilon-\epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}}} d(\epsilon - \epsilon_0) \quad (19)$$

where

$$\beta_2 = K_{\infty} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \sqrt{\frac{m}{\pi}} \frac{1}{4s^2} e^{\frac{\epsilon_0}{kT}}$$

This has been integrated by graphical means, and a series of curves for this purpose of the integrand, K_{ϵ} , against $\epsilon - \epsilon_0$ is shown in Fig. 1. The outer curve is the curve for infinite pressure, and the number near each curve gives the value of β'/p , where $\beta' = 3.16 \times 10^{-3} \beta_2$, ϵ and ϵ_0 being in calories per mole. The temperature used was 576° , n was taken as 11, and ϵ_0 as 54,000 calories per mole. These figures correspond to some of Hinshelwood and Thompson's experiments on propionic aldehyde. The ordinates represent the relative number of molecules having a definite energy and pressure which react in a given time. Due to the character of the function the value of the integrand decreases rapidly with high values of $\epsilon - \epsilon_0$, and although the curve theoretically extends to infinity, actually we can use a finite portion of it.

In evaluating the heat of activation from the temperature coefficient of the reaction rate in the case of Theory II, we note that here

$$\frac{d \log K_{\infty}}{dT} = \frac{\epsilon_0 + \frac{1}{2} kT}{kT^2} = \frac{U}{kT^2} \quad (20)$$

as shown by Rodebush²¹ since the rate at high pressures depends on the probability that a *single* degree of freedom have an energy greater than ϵ_0 .

We can now use the set of curves in Fig. 1 to justify the assumption we made that the actual rate of formation of molecules in a given energy range was to be calculated from the rate of loss which would exist under equilibrium conditions. The lower the pressure the less justified we would consider this assumption to be. Consider, therefore, the lowest curve of the set shown. A trifle over 11% of the area under it is to the

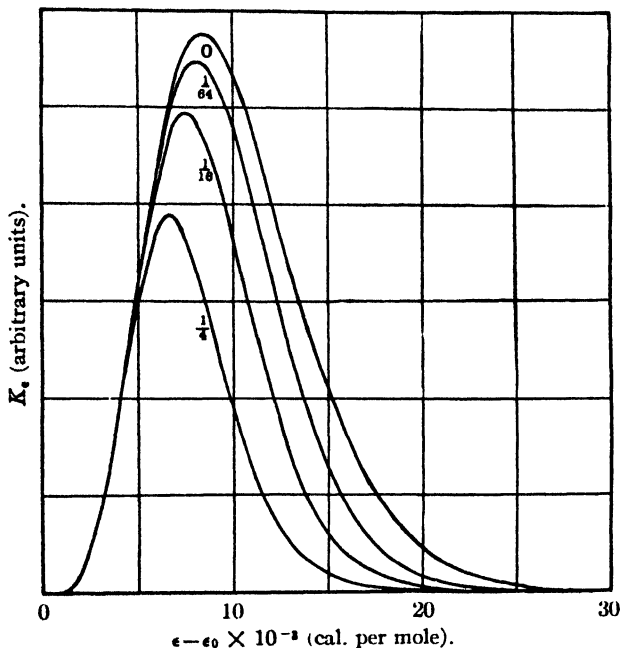


Fig. 1.—Curve $\beta'/p = 0$, relative area $(K/K_\infty) = 1.00$, $\beta'/p = 1/64$, $(K/K_\infty) = 0.84$; $\beta'/p = 1/16$, $(K/K_\infty) = 0.66$, $\beta'/p = 1/4$, $(K/K_\infty) = 0.44$.

right of the 11,000 mark. At $\epsilon - \epsilon_0$ equal to 5000 the concentration is about 8% of the equilibrium value. We now ask the question: How many of the molecules having an energy per mole of 65,000 cal. ($\epsilon - \epsilon_0 = 11,000$) were formed from molecules having an energy of more than 59,000 cal. per mole, and hence not present in approximately equilibrium numbers? To answer this let us use the principle of entire equilibrium and find what is the chance that a molecule of 65,000 cal. per mole energy should not lose more than 6000 cal. per mole at a collision with an average molecule (or that the other molecule should leave with more than 59,000 cal. per mole). We can do this if we assume that statistical equilibrium

²¹ Rodebush, *THIS JOURNAL*, **45**, 610 (1923).

is established between the various degrees of freedom of both molecules at a collision. If statistical equilibrium is not established at a collision, the error would be about the same for low- and high-energy molecules, and the chief result would be that only a fraction of the collisions would be effective in deactivation, which would merely mean that β_2/p would have to be multiplied by a constant factor. While this last point cannot be said to be strictly established, it is obvious that the calculation we propose to make will be a valuable indication of the validity of our assumption.

If two molecules, each having n degrees of freedom, collide, there are $2n$ degrees of freedom involved. The chance that one of the molecules with n degrees of freedom should have an energy between ϵ_2 and $\epsilon_2 + d\epsilon_2$ is

$$\Gamma\left(\frac{n}{2}\right) \left(\frac{\epsilon_2}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon_2}{kT}} \frac{d\epsilon_2}{kT} \quad (21)$$

The chance that the other molecule should have energy between $\epsilon' - \epsilon_2$ and $\epsilon' - \epsilon_2 + d\epsilon'$ is

$$\frac{1}{\Gamma\left(\frac{n}{2}\right)} \left(\frac{\epsilon' - \epsilon_2}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon' - \epsilon_2}{kT}} \frac{d\epsilon'}{kT} \quad (22)$$

By reasoning similar to that following Equations 12 and 13, the product of 21 and 22 is the probability that the total energy of the two molecules is between ϵ' and $\epsilon' + d\epsilon'$, while one of them has energy between ϵ_2 and $\epsilon_2 + d\epsilon_2$. But the chance that the two together have energy between ϵ' and $\epsilon' + d\epsilon'$ is

$$\frac{1}{\Gamma(n)} \left(\frac{\epsilon'}{kT}\right)^{n-1} e^{-\frac{\epsilon'}{kT}} \frac{d\epsilon'}{kT} \quad (23)$$

The product of Equations 21 and 22 divided by Equation 23 is the chance that if two molecules have an energy of ϵ' together, a certain one of them has an energy between ϵ_2 and $\epsilon_2 + d\epsilon_2$. Now we start with two molecules, one of which has an energy of 65,000 and the other the average energy or 9300 cal. per mole, the sum of which is ϵ' . We wish to find the chance that either of them should come out of the collision with an energy greater than 59,000 cal. per mole (ϵ''). We must double the expression [(21) \times (22)/(23)] to allow for either molecule having the energy, and integrate.

$$\frac{2\Gamma(n)}{\epsilon'^{\frac{n}{2}} \left[\Gamma\left(\frac{n}{2}\right)\right]^2} \int_{\epsilon''}^{\epsilon'} \left(\frac{\epsilon_2}{\epsilon'}\right)^{\frac{n-2}{2}} (\epsilon' - \epsilon_2)^{\frac{n-2}{2}} d\epsilon_2 \quad (24)$$

For the sake of simplicity, and since it can only cause the probability to come out greater than it should be, we will take ϵ_2/ϵ' as 1, and get

$$\frac{4\Gamma(n)}{n \left[\Gamma\left(\frac{n}{2}\right)\right]^2} \left(\frac{\epsilon' - \epsilon''}{\epsilon'}\right)^{\frac{n}{2}} = 0.081 \quad (25)$$

This seems small enough to justify our assumption as an approximation, especially when it is considered that the molecule we fixed attention on had considerably higher energy than the average reacting molecule.

Discussion of the Results in Connection with the Decomposition of Propionic Aldehyde

Either Equation 5 or 19 allows us to plot a curve for K against p . In order to fit the data one must have values of β_1 or β_2 and K_∞ which must be determined from the data, themselves. In this situation it is convenient to plot $\log K/K_\infty$ against $\log p$. In such a plot Theory I gives curves which are absolutely invariable in shape and are shifted horizontally by changes in β_1 . We can then plot the data in a similar fashion on transparent coordinate paper and attempt to effect a fit by moving the curve over the data. Since K_∞ from the data may be in error by 10 to 15% we may shift data and curves relatively to each other a short distance in the vertical as well as in the horizontal direction. The value of β_1 may be calculated from the final position of the theoretical curve, and assigning a reasonable value for s and knowing all quantities involved except n , we may find a value for n .

In Theory II a slight change in form occurs if n is changed. We must, therefore, assign a value of n in advance, and the value of β_2 which it is necessary to use in order to fit the data, and which is found by relative shifting of points and curve, as for Theory I, must agree with this value of n and the known values of the other quantities involved in the expression for β_2 ; however, because of the way in which the molecular diameter and heat of activation enter β_2 we have a leeway in this matter of several fold.

We have used the scheme outlined in constructing Fig. 2, which is for Hinshelwood and Thompson's data¹ at 576°. It will be seen that it is necessary to assign different values to K_∞ for the two theories, and that in either case the theoretical value of K_∞ is considerably higher than the highest experimental value of K . This suggests that information might be obtained not only from experiments at lower pressures, but also by experiments at higher pressures.

The value of K_∞ on Theory I is 0.020 from Fig. 2 (knowing the values of Hinshelwood and Thompson's constants). The value of β_1 used is 57 mm. of mercury. Using $s = 6 \times 10^{-8}$ and $U = 55,000$ from Hinshelwood and Thompson's temperature coefficient (see Equation 6), we find that the best value for n is 12, which checks with Hinshelwood's estimate.

The value of K_∞ on Theory II from Fig. 2 is 0.023. Using this, s as above, and $\epsilon_0 = 54,000$ (see Equation 20) we calculate that β_2 should be 1900 (n being taken as 11). The value of β_2 actually used is 4000, which is close enough, as a change of 1 in the value of n would introduce a larger discrepancy.

It will be seen that the data on the decomposition of propionic aldehyde does not allow us to decide which theory is better. We hope to be able to do this soon in the case of azomethane, experiments on which are now under way.

The curves for Theory I at different temperatures should practically coincide. On Theory II, this is not quite the case, but the effect is small (within experimental error). Hinshelwood and Thompson's data for 523°, the other temperature for which they give initial rate constants, fall similarly with reference to theoretical curves but they are displaced in the figure, a certain amount vertically corresponding approximately to the difference in the calculated²² and experimental values for high pressures in Hinshelwood and Thompson's table.²³

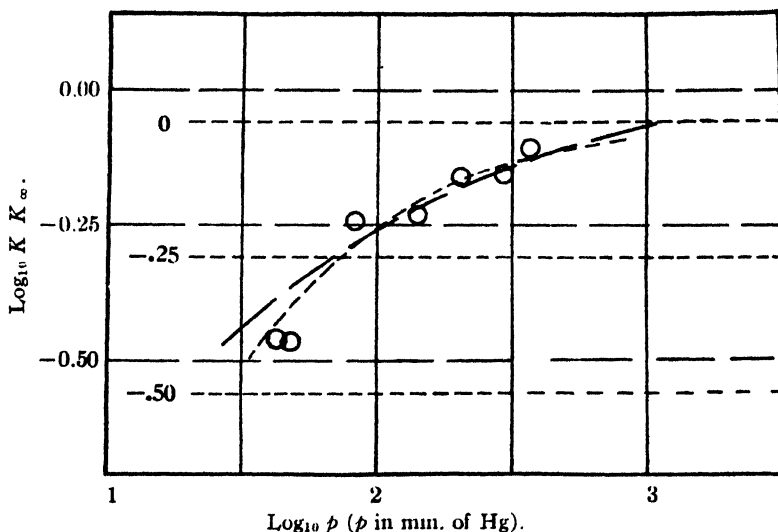


Fig. 2.—Theory I, - - - - -. Theory II, ———.

Other Theories

We may briefly dispose of the other theories mentioned on page 1618 as follows. One may go through a deduction similar to that given for Theory II. In each case this would seem to indicate that for a fixed total number of degrees of freedom this would give results intermediate in character to those of the two theories considered in detail, except (a) which gives exactly the same result as Theory II.

Summary

A collision theory of homogeneous gas-phase, unimolecular reactions at low pressures has been developed. Several possible forms of the theory

²² From the temperature coefficient and constants at other temperatures.

²³ Ref. 1, p. 228.

are suggested, and two of them carefully considered. These theories take account of the distribution of energy among the large number of degrees of freedom of the rather complex molecules that are known to decompose in unimolecular manner. They determine the way in which the reaction rate would be influenced by the initial pressure and can, therefore, be tested experimentally. All molecules which have a certain minimum total energy which can be calculated from the temperature coefficient are said to be activated. The rate of activation is calculated from the distribution of energy among molecules having n degrees of freedom, and by assuming that the rate of activation is equal to what the rate of deactivation would be under equilibrium conditions, and that each collision of an activated molecule results in deactivation.

When the pressure is high, most activated molecules are deactivated and but a small fraction react. At lower pressures an appreciable fraction of them react, and at very low pressures when most of the activated molecules react the reaction rate becomes very much smaller and bimolecular. By Theory I, the chance of reaction is independent of the excess of energy beyond that required for activation, and this leads to an equation of the form $K = K_{\infty} p / (p + \beta_1)$, where K is the rate constant, K_{∞} the rate constant at high pressures, p the pressure and β_1 a constant involving the number of degrees of freedom, the molecular diameter, the heat of activation, K_{∞} , etc.

Theory II requires not only that a molecule have a minimum total energy, but that such an activated molecule react only if it contains a certain minimum of energy in a particular degree of freedom. It is assumed that the internal energy may be repeatedly redistributed within the molecules between collisions. If a molecule has a large excess of energy beyond that required for activation, there will be a greater probability that this energy will get into a particular degree of freedom to cause reaction. An equation is derived which gives this probability. By fixing the number of degrees of freedom, etc., it is possible to determine the relative reaction rate at various pressures by means of a graphical integration.

The data on the decomposition of propionic aldehyde at various pressures are found to fit the theoretical curves of Theory I and Theory II about equally well. More accurate data extending over a wider pressure range are necessary to decide between the two theories.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 144]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. IV. DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM DICHROMATE ACCELERATED BY MANGANESE SALTS

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Previous studies have shown that the promotion effect noticed when two catalysts act simultaneously can be explained simply upon the basis of a change in the path of the related reactions which together produce the resultant catalytic effect, and that it is not necessary to introduce the conception of activation discussed by Pease and Taylor.² This change in the path was first demonstrated when it was shown that the copper which promoted the catalytic decomposition of hydrogen peroxide by ferric salts³ appeared as a new molecular species, namely, cupric acid. In a later study it was possible to show that the intermediate due to the catalyst decreased in concentration during promotion.⁴ This was in the system where the decomposition of hydrogen peroxide by potassium dichromate was accelerated by the presence of cobalt salts. While in this case it was not possible to identify the intermediate due to the promoter, nor to follow the formation of this substance and to show the dependence of its formation upon the disappearance of some of the intermediate due to the catalyst, nevertheless it was shown that the shape of the promotion curve followed closely an equation which had been derived governing this effect. This agreement with theory showed that catalysis obeys the law of mass action as well as do other reactions.⁴

Other promoters have been found for this reaction, so the studies were extended further to test the hypothesis. The system chosen was the one where manganous chloride acts as a promoter for potassium dichromate in decomposing hydrogen peroxide. Although the experimental results are not altogether free from complications, the interpretation of the data forms an interesting addition to and confirmation of the earlier work.

Experimental Methods

The method of experimentation⁵ is practically the same as that used in previous studies.

A special reaction flask containing the solution of hydrogen peroxide is held in the thermostat by means of a suitable clamping device. This flask is connected by small-bore glass tubing to a gas buret maintained at the same temperature as the thermostat.

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² Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

³ Robertson, *THIS JOURNAL*, **47**, 1305 (1925).

⁴ Robertson, *ibid.*, **48**, 2072 (1926).

⁵ Walton, *Z. physik. Chem.*, **47**, 188 (1904).

When thermal equilibrium is attained, a capsule containing the catalyst is dropped into the flask which is then shaken vigorously, and readings of the amount of gas evolved are made at convenient intervals. The method has proved rapid and accurate. The thermostat, which has been improved by the addition of an oscillating contact on the thermoregulator, gives a temperature regulation never varying over 0.01° , and with an average deviation of $\pm 0.003^\circ$ for an hour in spite of the large radiating surface of the water jacketed gas burets.

Promotion by Manganese Chloride at Low Concentrations.—The manganous chloride used in this study was carefully purified from the best available material. A solution of the salt was first treated with a quantity of freshly precipitated, well-washed manganous carbonate to remove iron present in large amounts. The solution was then filtered, saturated with hydrogen chloride and allowed to crystallize. This recrystallization was repeated. The salt was then crystallized from water, sucked dry upon a Büchner funnel and dried in a desiccator for several hours. This process yielded a moisture-free product which gave a clear solution neutral to litmus. The catalyst solutions were made by appropriate dilutions of a standard solution made from this material.

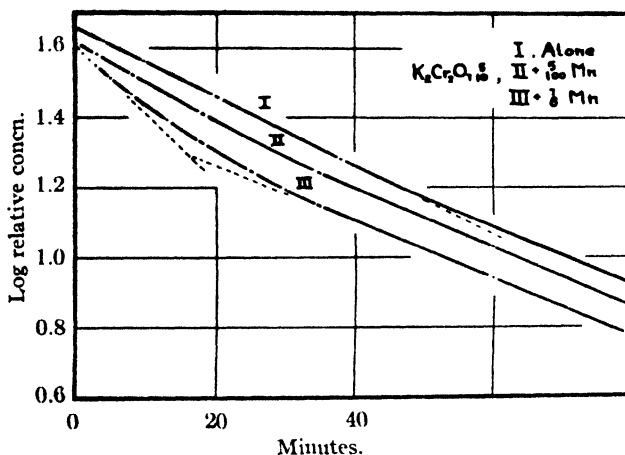


Fig. 1.—Concn.-time curves of typical examples.

The manganous chloride is rather a poor catalyst when used alone, giving a reaction constant of the order of 5 for a concentration of $0.04 M$. Its effect when used alone is autocatalytic, but when the salt is used as a promoter the reaction as a whole is not. Instead of being strictly of the first order, as with cobalt for a promoter, the reaction constants decrease with time in the manner shown in Fig. 1, where the logarithms of the concentration ratios are plotted as ordinates against the time in minutes as abscissas. The velocity constant for the reaction remains unchanged at first, as shown by the slope of the curve, but later decreases. The curve appears to merge into another approximately straight line.

More concordant results were obtained upon repetition of the experiments when the catalyst was added to the solution rather than the reverse. It was necessary to adopt this method although it involved a more

exacting technique and made the preparation of the catalyst solutions somewhat less accurate.

This curve was studied critically by plotting the results on a large scale. It appeared that the curve was made up of two superimposed exponential functions, which will be discussed later. This fact indicates the simultaneous presence of two first-order reactions in the catalytic process.

Catalytic Nature of the Reaction

The fact that the relationships were complicated and that several effects were present at the same time led to the suspicion that the reaction might not be truly catalytic in its outcome. This is disproved by the fact that when a mixture 0.0, 0.0005, 0.089 and 0.445 *M* in manganous chloride as promoter ran to completion (nine hours) the volumes of gas evolved were 45.10, 45.55, 45.55 and 45.65 cc., respectively. These differences are less than the usual, except for the first case where the reaction possibly had not enough time to complete its course. Since the calculated amount of oxygen necessary to oxidize one millimole per liter of bivalent metal to the quadrivalent state for a sample of 25 cc. is 0.0311 cc. of gas, it is seen that the reaction oxidizes very little manganese if any, although manganese salts are notoriously easily oxidized if the solutions are not neutral, even air effecting this change. Neither is an appreciable amount of the dichromate reduced, as shown by the color of the solution. From these facts it may be concluded that when the manganese and dichromate act together the reaction is still purely catalytic in character, these substances being left unchanged in amount and kind at the end of the reaction.

Preliminary experiments have shown that the reaction with manganese alone was somewhat autocatalytic in character. It was suspected that this effect might be due to the alkali ground off the flasks by the beads,

TABLE I
EFFECT OF CONDITIONS UPON THE CATALYSIS BY MANGANESE CHLORIDE

Concn. of MnCl ₂ , <i>M</i>	Time	<i>x</i>	<i>K_R</i>	<i>x</i>	<i>K_R</i>	<i>x</i>	<i>K_R</i>	<i>x</i>	<i>K_R</i>
0.025	0	0.00	..	0.00	..	0.00	..	0.00	..
Bakelite	7	.06	0.35	.06	0.57	1.0	0.46	.02	0.86
beads	32	.27	.31	.20	.50	.15	.75	.12	1.15
	184	1.76	.37	1.13	.48	.91	.77	.62	1.05
	∞	111.6	..	55.8	..	27.9	..	14.0	..
	Time	<i>x</i>	<i>K_R</i>	Time	<i>x</i>	<i>K_R</i>			
0.040	0	0.00	..	0	0.00	..			
	7	.55	4.2	6	.37	3.3			
Glass beads	13	1.15	4.5	13	1.25	5.1			
	23	2.50	5.7	18	1.97	5.8			
	195	28.10	8.9	106	17.25	9.6			
	∞	85.5	..	∞	83.7	..			

and measures were taken to surmount this difficulty. This was accomplished by using new, unscarred Pyrex flasks and by substituting bakelite beads and capsules for glass. These substitutes served their purpose well since this material is one of the most resistant toward chemicals. Although it was somewhat brittle, the bakelite secured for this purpose could be worked in the lathe after a few trials. The capsules were apparently unaffected by the reagents used and gave determinations which checked well with those determined in the usual way.

The data are recorded in Table I for runs made with the new equipment. It can be seen by reference to this table that the reaction between hydrogen peroxide and manganous chloride gives good first-order constants. They show but a slight trend with time and are quite small, all this in contrast to the case where the reaction is complicated by the presence of traces of alkali derived from the glass.⁶

Spitalsky also has shown that the reaction between hydrogen peroxide and potassium dichromate⁷ is purely catalytic for low concentrations of this salt.

The catalytic nature of the two component reactions has now been established and it has been shown that when the reactions occur together the reaction is still catalytic. The promotion reaction may, therefore, be considered in the same manner as in previous studies and the conception of the steady state may be utilized as has been done before.

Interpretation of the Data

As stated previously, the shape of the curve shows the presence of two superimposed first-order reactions. This condition in cases of promotion was postulated previously,⁸ but due to the nature of the reactions it has not been possible to resolve the effect into its component parts. The previous inability to divorce the effects which cause promotion is no doubt due to the fact that either the amount of the hydrogen peroxide involved in the reaction which causes the promotion was small, or the rate of this promoting reaction was only slightly faster than the reaction which it supplanted; or it may have been that both the amount of substrate involved and its rate of reaction were small. In any event the effect, as a whole, was so small that when it was superimposed upon the regular reaction it did not change the *nature* of the concentration-time curve to such an extent that it could be detected by analysis of the experimental data.

⁶ This alkali does not cause any disturbance when manganese is used in the presence of dichromate, since a small amount of the catalyst is converted into the chromate and the reaction of the solution remains unchanged. The usual concentration of alkali produced was shown by experiments performed for another purpose to be in the order of 10^{-4} *M*. This is 0.2% of the concentration of the catalyst.

⁷ Spitalsky, *Z. anorg. Chem.*, 53, 187 (1907).

⁸ Ref. 4, p. 2076.

The difficulties of resolving the promotion effect into its parts are much less formidable in the case where manganese is used as the promoter. Since the curve consists of two superimposed exponential functions, it is necessary to resolve the promotion effect into two parts. This may best be done by considering the chemical reactions involved. Therefore, the exponential expression is written in the logarithmic form commonly used by chemists, $Kt = \log f/f - x_1 + \log d/d - x_2$ and the rate expressed in the following manner

$$K = 0.4343 K \times 10^4 = \frac{F}{t} \log \frac{f}{f - x_1} + \frac{D}{t} \log \frac{d}{d - x_2} \quad (1)$$

where f is the amount of hydrogen peroxide taking part in the non-promoted reaction, d the amount of hydrogen peroxide involved in the promotion reaction and F and D are the rates of these respective reactions. Thus stated, F and D are not the same constants as those used in the previous paper. These values are related to the specific velocity constants, while those used before⁸ represent the gross effect. Here the effects causing promotion have been resolved into their components. The values x_1 and x_2 are variables comparable to x . Their significance will be apparent by looking at the sample calculation in Table II.

A number of runs was made with the concentration of the potassium dichromate fixed at 0.0005 M and with the manganese varying in concentration between 0.000001 and 0.145 M . Upon inspection it appeared that the relationships were different for the concentrations of manganese above 0.001 or 0.002 M than for those below. The treatment for the present is confined to the region between 0 and 0.0025 M in manganese. The higher concentrations will be considered later.

Upon inspecting log concentration-time graphs, similar to those shown in Fig. 1, in which various amounts of manganese were used, it appeared that the last portion of the curve had the same slope in all cases, while only the first portion showed a variation due to the promotion effect. Since the last portions of the curves for systems exhibiting promotion have the same slope as the unpromoted curve, it indicates that the primary reaction upon which the promotion effect is superimposed is not changed in rate by the presence of the promoting reaction. In preliminary studies it had been thought that this rate might be changed, but if a variation does occur it lies within the limits of experimental error. Therefore, it was assumed that the effect due to the second reaction could be obtained by subtracting the effect due to an unpromoted reaction from the observed values. Upon proceeding to calculate the results to determine the nature of this superimposed reaction a difficulty becomes apparent, since the unpromoted reaction, when followed over a long period of its life, begins to decrease in velocity although the reaction is pseudo-unimolecular and should, therefore, give good velocity constants. An

examination of Spitalsky's data shows the presence of a similar effect.⁷ This cannot be accounted for by assuming that there is a diminution of the concentration of the catalyst due to the reduction of chromium, since this effect has been shown to be absent by means of chemical analysis. Again, a direct test shows that the effect cannot be due to the solubility of the glass ground off by the beads.

In order to make the calculations of the superimposed reaction more easily interpreted, the velocity constant for the early part of the reaction was arbitrarily set at 100 (later it dropped to 90). It happens that the "break" for all the log concentration-time curves comes in the region where the reaction rate for the non-promoted reaction is still 100, so this assignment of values is quite justified. Therefore, when a line representing a reaction rate of 100 is drawn tangent to the curve passing through the points representing the experimental values and is extrapolated back to

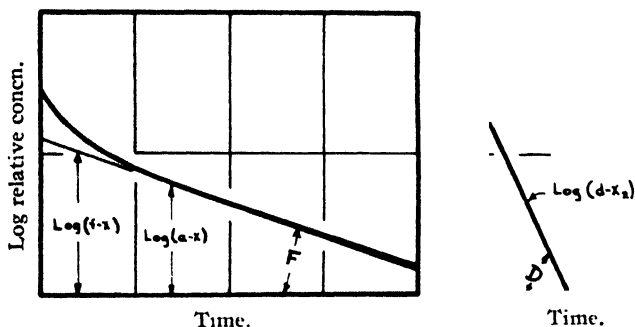


Fig. 2.

zero time or the beginning of the reaction, the intersection of this line with the zero ordinate represents the concentration of the hydrogen peroxide, f , involved in the non-promoted reaction at the beginning. The valid assumption must be made that the velocity constant F is the same for this slightly lower concentration of hydrogen peroxide. The difference between this calculated concentration and the original concentration of hydrogen peroxide represents the amount of hydrogen peroxide going through the reactions which cause the promotion. Fig. 2 represents the operation schematically. This difference is obtained by reading off the logarithms of the extrapolated line; these values are called $\log(f - x_1)$ and are recorded in the sample calculation in Col. 3. The numbers $(f - x_1)$ are now entered in Col. 5 and subtracted from the values $(a - x)$, which are the actual concentrations. This difference is called $(d - x_2)$, where d is the concentration of hydrogen peroxide which at the beginning of the reaction enters into the promotion reaction. In order to see how the promotion reaction proceeds, the logarithms of $(d - x_2)$ are plotted against time in the same manner as for any other first order

reaction. The points fall on a straight line, the slope of which gives the reaction rate of this reaction. This slope is the D of Equation 1.

A synthetic curve formed from the constants obtained approaches the original curve for this region to less than 0.1 cc., and seldom departs farther than 0.2 cc. Considering the uncertainties attending the exact determination of the end-point and the time of mixing, the values are very satisfactory indeed. In the sample calculations shown in Table II, the calculated and observed values of $(d - x_2)$ are recorded in the last columns.

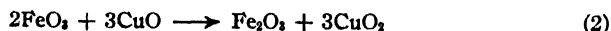
At the beginning of the reaction several minutes must be allowed for the time of mixing and the attainment of the new steady state which, however, is more rapid in this case than when cobalt is used for the promoter. It is necessary to apply a small correction in order to determine the most probable value of d . This is done by a back extrapolation on the graph of the buret readings, which gives the actual time when the reaction began. The zero time is marked on the graph of $\log(d - x_2)$ and the corrected value is then read off from the intersection of these lines.

TABLE II
SAMPLE CALCULATIONS
 F , 100 by definition; f , 31.1 cc.; D , 570; d , 8.9 cc. or 21.9%

	x	$\log(f - x_1)$	$(a - x)$	$(f - x_1)$	$(d - x_2)$, obs. ^a	$(d - x_2)$, calcd. ^a
0	2.05	1.496	40.65	31.33	9.32	8.50
1	4.75	1.486	37.95	30.62	7.33	7.30
2	6.20	1.476	36.50	29.92	6.58	6.50
3	7.80	1.466	34.90	29.24	5.66	5.65
5	10.35	1.446	32.35	27.93	4.42	4.30
8	13.70	1.416	29.00	26.06	2.94	2.95
13	17.95	1.366	24.75	23.23	1.52	1.50
18	21.42	1.316	21.28	20.70	0.58	0.77
25	25.00	1.246	17.70	17.62	0.08	0.03
30	27.00	1.196	15.70	15.70	0.00	..
35	28.70	1.146	14.00	14.00	0.00	..
92	37.80	...	4.90
∞	42.70

^a d corrected to zero time, 8.9.

In Fig. 3 the values of d are plotted against the concentration of promoter in millimoles per liter. The unit of measurement is the percentage fraction of the hydrogen peroxide present at the beginning of the reaction. The maximum in the curve may have some relation to the stoichiometric ratios involved in the promotion reaction, as seems probable from previous studies with copper as a promoter for iron. At very low concentrations this system showed a maximum in the curve where the "promotion factor" was plotted against the mole fraction of total heavy metal present. This maximum corresponded to a molar ratio which agreed well with the reaction³



which was followed by a very rapid reaction which produced the accelerating effect. This concept is based on the reasonable supposition that the maximum effect should be obtained in the promotion reaction when the reactants are present in ratios corresponding to their reacting masses.⁹

Further studies were not carried out to test this point since the entrance of disturbing effects due to the presence of a reaction which predominates at higher concentrations of manganese renders such experiments of dubious value. If the maximum be at 0.001 *M*, it indicates that the intermediate is manganese with a valence of three, since the system is one using potassium dichromate at a concentration of 0.0005 *M*. Equation 3 represents the reaction; the formula of the intermediate due to the promoter is written HMnO_2 here only to depict the trivalence of manganese.

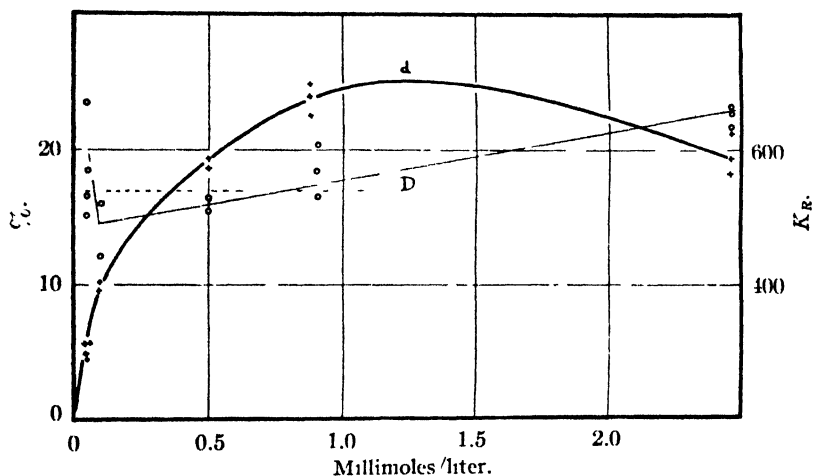


Fig. 3—Relation between *d*, *D* and the concn. of promoter.

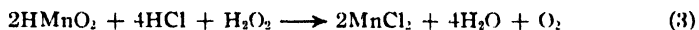
Spectrographic studies have been made with solutions of manganese salts of varying valence.¹⁰ While these measurements are only of qualitative value they show that this method cannot be used to determine whether the valence is three or four.

The values of *D*, the reaction rate for the promotion reaction, are also plotted in Fig. 2. The scale of ordinates for this series is placed on the right of the graph. The points, excepting the first few corresponding to very low concentration of promoter, fall upon a straight line.

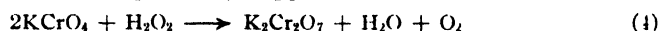
⁹ A maximum was not found in the promotion curve when cobalt was used as the promoter. It seems probable that this effect can only be expected when the concentration of the second intermediate due to the promoter is substantially equal to the concentration of the first intermediate due to the catalyst. Otherwise the "cyclic" nature of the reactions obscure the relationship.

¹⁰ Jaeschke and Meyer, *Z. physik. Chem.*, **83**, 281 (1913).

In those experiments, the duration of the superimposed reaction is so very short compared to the time for the others that the time of mixing becomes a large factor, and errors are to be expected. It was impossible for this reason to assign any values at all when 0.000001 *M* manganese was employed as the promoter. The variable time of mixing no doubt accounts for the variable values in this part of the curve. The slope of the line is so slight that it seems logical that it might be zero. In this case it would represent a rate which is related to the specific velocity constant of some rapid reaction such as



This is the reaction which gradually supplants the reaction



normally taking place in the non-promoted reaction; the difference between these rates of reaction is apparent in the acceleration of the reaction as a whole. The reaction represented by Equation 3 can take place because of the "transition" reaction shown in Equation 5.



This transition reaction is more rapid than the others; for the sake of simplification its rate will be considered as instantaneous until a method is found by which it may be evaluated. This assumption is necessary in order that the equation of promotion (and negative catalysis, also) may be developed quantitatively, using the concept of the steady state as the basis for calculations.

The slight slope of the line passing through the values for *D* is due to traces of the reaction which predominates at the higher concentrations of manganese; the probable interference of the reaction has been noted before.

It was not deemed necessary to study the effect of the hydrogen-ion concentration further, since an investigation of the effect of cerous salts as promoters promises to cast much more light upon this relationship.

Effect of Higher Concentrations of Manganese

It was noticed early in the investigation that the larger amounts of manganese caused the reaction to follow a much more complicated course. Therefore, a number of experiments were devised to determine more about the nature of this complicating reaction. The results are not completely reproducible and do not lend themselves to exact treatment, but they are definite enough so that valid conclusions may be drawn from them.

The first step was to determine how the promotion reaction was influenced by changes in the concentration of the hydrogen peroxide. When a reaction mixture 0.0005 *M* in potassium dichromate was promoted with

either 0.0025 or 0.02 *M* manganese, the value of *d* decreased one half or one fourth for a similar decrease in the concentration of hydrogen peroxide. However, doubling the concentration of hydrogen peroxide more than doubles the value of *d*. In both cases the value of the reaction constant *D* is substantially the same, although slightly larger with 0.02 *M* manganese.

Thus it is seen that the amount of the intermediate due to the promoter is proportional to the amount of hydrogen peroxide used. Although the reaction satisfies the equation for a first-order process, it is only pseudo-unimolecular, being actually a real second-order reaction. This fact was suspected earlier in the investigation, so care was taken that the experiments summarized in Fig. 3 were performed with hydrogen peroxide of exactly the same concentration. To accomplish this end the runs were made consecutively within a few days, during which time the sample of peroxide changed but little in concentration.

These experiments represent a steady-state condition, as shown by the fact that the results are the same with a concentration of 0.00001 *M* manganese whether the concentrated peroxide is dropped into the catalyst or whether a concentrated catalyst solution is dropped into the dilute peroxide. This condition does not exist when 0.0005 *M* manganese is used, indicating that the interfering reaction noted at higher concentrations of manganese is not a steady-state condition. Therefore all the experiments in Fig. 3 were performed with dil. hydrogen peroxide, so the effect of the interfering reaction would be minimized.

When the concentration of manganese is 0.09 *M* or more, the experimental results cannot be consistently presented as in the previous case. The reaction does not follow either a first- or second-order equation. Although the effects are very complicated and practically impossible to resolve, it seems probable that the high concentrations of intermediate due to the catalyst present before the steady state is attained, oxidize some of the manganese to a form which is reduced at a different rate from the intermediate normally formed by the manganese.

By determining the time required to decompose various fractions of the hydrogen peroxide present and taking the reciprocals of these values, it is possible to gain an insight into the course of the reactions. These values should be constant for a first-order reaction and should vary directly with a second-order reaction.

When the concentration of manganese is 0.0025 *M*, the reciprocals increase somewhat, as shown in Fig. 4. The solid lines represent 0.0025 *M* and the dotted lines 0.09 *M* manganese added to the dichromate. By this slope in the line, the presence of the complicating reaction detected before may again be noted when the concentration of manganese is 0.0025 *M*, but when 0.09 *M* is used this complicating effect, instead of being larger,

disappears. The dotted lines have practically no slope and show that by the half-life criterion the reaction is unimolecular. The reaction doubtless is not so simple. Considerations based upon spectrographic studies indicate that this reaction involves the formation and decomposition of a permanganate, and it is not to be expected that this process is unimolecular.

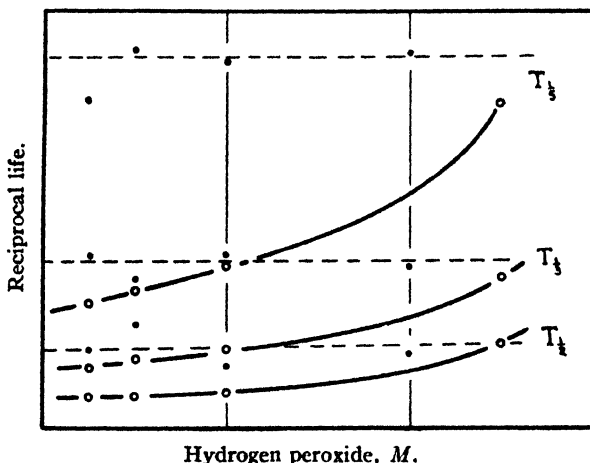


Fig. 4.

Spectrographic Studies

The study of the absorption spectra of solutions undergoing catalytic change has proved a powerful tool in this series of studies upon catalysis and promoter action. The first application was to show the presence of an intermediate compound formed from the catalyst and to show its chemical nature by comparison with a solution containing a substance of known composition. In another case the presence of the "promoter" in a new form was shown by this method. In a third study the "first intermediate" was shown to decrease in concentration when the catalytic change was promoted.

Optical methods are almost essential in studying intermediate compounds, which are by definition unstable, and in very few cases can be handled by the time-honored methods of the analytical chemist. Bray and Livingston¹¹ were able to isolate and measure quantitatively the intermediate in the reaction which they were studying, because of the low rate of the reactions involved.

The effect of manganous chloride upon the concentration of the intermediate due to the catalyst is very large indeed, as shown by Fig. 5. One millimole per liter reduces its concentration about 75% and 2.5 millimoles per liter practically removes all trace of the substance. The

¹¹ Bray and Livingston, *THIS JOURNAL*, **45**, 1256 (1923).

absorption now shows only the presence of potassium dichromate; there are no new absorption regions in the visible, hence the nature of the new compound of manganese cannot be determined by this method.¹⁰

When more manganese is used, for example, 0.02 *M*, the results vary with time; a steady-state condition does not prevail. In Fig. 6 the results are shown graphically. A maximum has appeared in the curve in a region which gave complete transmission when 0.0025 *M* manganese was present. This maximum corresponds almost exactly to the peak of the absorption curve for a solution of potassium permanganate. If this be true, the concentration of permanganate is about 0.000005 *M*. These results are calculated from the molar extinction coefficient for potassium permanganate obtained by other workers.¹² Their value

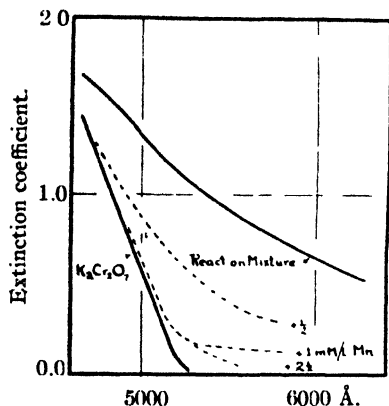


Fig. 5.

Effect of promoter upon absorption spectra.

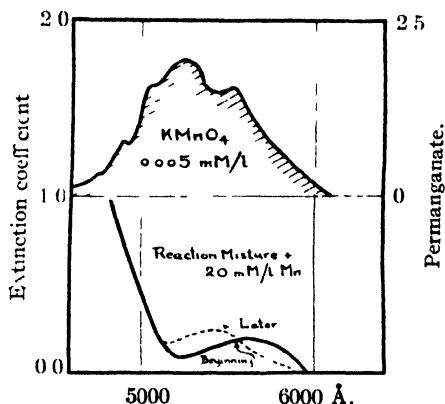


Fig. 6.

agrees well with one obtained by the use of diluted volumetric solutions of known oxidimetric value. This concentration of manganese as permanganate is 2.5×10^{-4} of that added as the promoter. It appears that the formation of permanganate is the cause of the complicated behavior found in some of the reactions.

This vanishingly small concentration of intermediate, a concentration which probably could only be detected by spectrographic means, indicates the necessity of investigating very closely the course of reactions before postulating the mechanism.

This research is based upon preliminary observations noted in studies carried on at the University of Wisconsin with Professor J. H. Walton. The final work was conducted at the California Institute of Technology and was aided by a grant made to Professor A. A. Noyes by the Carnegie Institution.

¹² Hagenbach and Percy, *Helv. Chim. Acta*, **5**, 461 (1922).

Summary

1. The catalytic decomposition of hydrogen peroxide by potassium dichromate is promoted by manganese salts. The reaction does not follow a simple unimolecular course.

2. The nature of the separate reactions has been investigated and discussed. Anomalous effects due to the solubility of the glass capsules and beads were avoided by the use of bakelite.

3. The promotion effect has been shown to consist of two superimposed reactions. The results agree with the explanation previously advanced for the relations between promoter and catalyst, and by resolving the promotion effect into two parts, one related to the concentration of intermediate due to the promoter, and the other, a rate related to the specific velocity constant of the promotion reaction, the interpretation offers a striking confirmation of the earlier work.

4. The addition of promoter causes the diminution of the concentration of the first intermediate. In the simpler reaction the nature of the intermediate due to the catalyst is not known definitely. When the concentration of manganese is higher, the relation is much more complex. The intermediate in this case is probably a permanganate, as shown by spectroscopic studies.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE ATOMIC WEIGHT OF SCANDIUM¹

BY NICOL HAMILTON SMITH

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Introduction

Until 1919 there had been considerable doubt as to the true value for the atomic weight of scandium. The atomic weight adopted by the International Committee on Atomic Weights was 44.1, which was considered to be a representative value based upon determinations made by previous investigators. These investigators had employed the usual sulfate method and had obtained values ranging from 43.90 to 45.23 as follows. Cleve, 44.96;² Nilson, 44.13;³ Meyer and Winter, 44.94;⁴ Meyer and Goldenberg, 44.09;⁵ Meyer and Schweig, 45.23.⁶

¹ From a thesis done in cooperation with Hiram S. Lukens, and submitted by Nicol H. Smith, in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania.

² Cleve, *Compt. rend.*, **89**, 419 (1879).

³ Nilson, *ibid.*, **91**, 56, 118 (1880).

⁴ Meyer and Winter, *Z. anorg. Chem.*, **67**, 398 (1910).

⁵ Meyer and Goldenberg, *ibid.*, **102**, 12 (1912).

⁶ Meyer and Schweig, *ibid.*, **108**, 303 (1919).

Such was the information concerning the atomic weight of scandium prior to Hönigschmid's series of determinations in 1919.⁷ He determined the ratio of scandium bromide to silver and from this value obtained for the atomic weight a mean value of 45.099 ± 0.014 , his values ranging from a minimum of 45.054 to a maximum of 45.122. Hönigschmid's scandium bromide was contaminated with small quantities of scandium oxide, formed by the action of scandium bromide on the quartz apparatus at the high temperature of sublimation. (On this account he had to apply a correction to every determination.

Since scandium chloride sublimes at a much lower temperature (850°) its action on the quartz apparatus, if any, should be very slight. Therefore, the ratio of scandium chloride to silver should give a better method for the determination of the atomic weight of scandium, even though the nephelometric end-point is not as sharp as in the bromide to silver ratio.

Purification of Scandium Oxide

The scandium oxide used in this investigation was obtained from a sample of scandium oxalate on hand in this Laboratory. In order to test the purity of this oxide a preliminary determination of the atomic weight was made. From the ratio of scandium oxide to scandium sulfate, the value of 45.29 was obtained, and from the ratio of scandium chloride to silver the values of 45.16 and 45.28 were obtained. These values indicated that the scandium oxide was reasonably pure to begin with. However, this fairly pure oxide was subjected to two methods of purification: first, by means of ammonium fluoride, and second, by means of ammonium tartrate.

Purification by Means of Ammonium Fluoride.⁸—The scandium oxide obtained by igniting scandium oxalate was dissolved in redistilled hydrochloric acid and evaporated to a sirupy consistency on the water-bath in a platinum dish. The solution was then diluted and any undecomposed oxide filtered out. The clear solution was then treated with redistilled ammonium hydroxide until the excess of acid was neutralized. This clear solution was then poured slowly with stirring into a hot solution of ammonium fluoride (using 8 to 9 g. of ammonium fluoride for every gram of scandium oxide). A gelatinous precipitate of scandium fluoride is first formed but this dissolves in the excess of ammonium fluoride. The solution was kept hot for about an hour on the water-bath, then filtered through a platinum funnel into another platinum dish. The residue should consist of the fluorides of thorium and the rare earths. The filtrate contained the complex fluoride of scandium and was evaporated almost to solidification. The residue, consisting of ammonium scandium fluoride and an excess of ammonium fluoride, was then treated cautiously with concd. sulfuric acid and evaporated slowly to fuming, first on a water-bath until all hydrofluoric acid had been expelled, and then on a hot-plate, taking care to prevent bumping and loss by spattering. Owing to the large excess of ammonium sulfate, the double ammonium scandium sulfate separated out. In order to avoid using a large volume of water to take this into solution, the greater

⁷ Hönigschmid, *Z. Elektrochem.*, **25**, 91 (1919).

⁸ Meyer and Wassjuchnow, *Z. anorg. Chem.*, **86**, 257 (1914).

part of the ammonium salts was volatilized by heating. The residue was treated with a small amount of concd. hydrochloric acid and heated. The scandium sulfate could then be easily dissolved in a small amount of water.

The solution was filtered free from any basic salt and ammonia gas was passed into the clear filtrate. The precipitated scandium hydroxide was filtered and washed free from ammonia with hot, redistilled water and then dissolved in pure, redistilled nitric acid, using only a very slight excess. An excess of pure, recrystallized oxalic acid was then added to the solution, heated almost to boiling and allowed to stand for 24 hours. The precipitated scandium oxalate was then filtered on a Büchner funnel, washed with pure water, sucking dry after each washing. The dried scandium oxalate was then ignited to oxide in a platinum dish. The oxide thus obtained was pure white and was supposedly free from cerium and yttrium earths and thorium.

This purified oxide was again dissolved in redistilled hydrochloric acid, the excess of acid removed by evaporating almost to dryness and the above purification with ammonium fluoride repeated. Scandium hydroxide was again precipitated by passing ammonia into the scandium sulfate solution. After thoroughly washing the scandium hydroxide, it was transposed to oxalate by boiling with a solution of oxalic acid. After standing it was filtered, washed thoroughly, dried and ignited to oxide. The oxide obtained was pure white and after two treatments with ammonium fluoride was considered to be free from thorium. This was called Sample I.

Purification by Means of Ammonium Tartrate.⁸—The scandium oxide was dissolved in redistilled hydrochloric acid and the excess of acid removed by evaporation on the water-bath to a sirupy consistency. The solution was diluted and any excess of acid removed by neutralization with redistilled ammonium hydroxide. The neutral scandium chloride solution was then poured very slowly with vigorous stirring into 750 cc. of a 15% solution of pure ammonium tartrate. The solution was filtered, since a slight precipitate was formed. The clear filtrate was heated to boiling and freshly distilled ammonium hydroxide added to the boiling solution until the solution was faintly ammoniacal. The scandium separated as the difficultly soluble scandium ammonium tartrate, thorium remaining in solution. The solution was digested for 15 minutes and the scandium ammonium tartrate filtered out, washed with a dilute solution of ammonium tartrate, dried and ignited to scandium oxide.

This oxide was again dissolved in pure hydrochloric acid, the excess of acid removed by evaporation and the ammonium tartrate purification repeated. The pure scandium ammonium tartrate was again ignited to oxide and dissolved in hydrochloric acid. Ammonia was then passed into the hot, diluted solution and the precipitated scandium hydroxide filtered out, washed well with pure hot water, sucking dry after each washing, and then converted to oxalate by boiling with a solution of oxalic acid in slight excess. After standing for 24 hours the scandium oxalate was filtered, washed with pure water, dried and then ignited to oxide. The oxide obtained was pure white and was considered to be free from thorium. This was called Sample II.

Purification of Other Materials

Silver.—The silver used in these analyses was prepared according to the method outlined by Richards and Wells.⁹

Silver chloride was precipitated from twice recrystallized silver nitrate by redistilled hydrochloric acid and then reduced by heating with sodium hydroxide and glucose solution. The silver oxide and silver thus obtained was fused on a block of pure sugar carbon. After solution of this silver in pure, redistilled nitric acid, it was again precipi-

⁹ Richards and Wells, *THIS JOURNAL*, 27, 459 (1905).

tated by warming the solution with a solution of pure ammonium formate, prepared by passing ammonia into redistilled formic acid. The silver was then fused on a block of pure lime before the blast lamp, and the silver bars thus obtained scrubbed with sea-sand, etched with dil. nitric acid, washed with dil. ammonium hydroxide and finally with pure water. Part of this silver was dissolved in pure nitric acid and used as the electrolyte; the other part of the silver was used as the anode and pure silver was deposited on a cathode consisting of a platinum wire. The silver crystals thus obtained were washed with pure water and fused in a pure lime boat in a current of hydrogen. The buttons obtained were washed with water, scrubbed with sea-sand, then etched with dil. nitric acid, washed with dil. ammonia and finally with pure water. The buttons were then cut into suitable sizes and heated to 400° in a vacuum and kept over potassium hydroxide until used. All precautions were taken for the purification of the materials used as prescribed by Richards and Wells.

Nitric Acid.—Concd. nitric acid was redistilled, the middle portion being collected, and was tested in a nephelometer to prove the absence of halogen.

Hydrochloric Acid.—Concd. hydrochloric acid was diluted and redistilled, the middle portion being collected.

Oxalic Acid.—Oxalic acid was recrystallized thrice from solution, acidified with hydrochloric acid and finally once from pure water, centrifuging after each crystallization.

Ammonium Tartrate.—Ammonium tartrate was recrystallized twice from pure water, centrifuging after each crystallization.

Ammonium Fluoride.—The ammonium fluoride used was the purest that could be obtained. Upon examination it yielded only a trace of non-volatile material and for this reason was not subjected to a purification.

Water.—The laboratory distilled water was redistilled from alkaline permanganate. Water to be used for the nephelometer was distilled once more from dil. sulfuric acid. The condensers were made of pure block tin fitted to Pyrex flasks with constricted necks. The water was collected in Pyrex flasks and was used immediately.

Carbon Tetrachloride.—Pure carbon tetrachloride, sulfur-free, was dried for two weeks over anhydrous calcium chloride and then fractionated, collecting the middle fraction within 0.1° .

Preparation of Anhydrous Scandium Chloride

Anhydrous scandium chloride has been prepared by the action of a mixture of sulfur monochloride and chlorine on the heated oxide.¹⁰ The scandium chloride used in this investigation was prepared by the action of carbon tetrachloride on scandium oxide at a temperature of 750 – 800° . At first, attempts were made to prepare the chloride by the action of chlorine on an intimate mixture of scandium oxide and sugar carbon, but the yields of anhydrous chloride obtained were so small that this method of preparation was abandoned. The action of carbon tetrachloride on the heated oxide proceeds very smoothly. The apparatus used for the preparation of anhydrous scandium is a bottling apparatus, as shown in Fig. 1.

It consists of a quartz tube A, 36 cm. long with a side tube (c) 22 cm. long and 2 cm. wide. This quartz tube was ground to fit a Pyrex end B, 19 cm. long with two side tubes (a) 10 cm. long to hold the weighing

¹⁰ Matignon and Bourion, *Compt. rend.*, 138, 631 (1904).

bottle and (b) 12 cm. long to hold the stopper for the weighing bottle. The quartz boat containing scandium oxide was placed in the quartz side tube (c) and the air completely displaced from the apparatus by a stream of pure nitrogen. The nitrogen was prepared according to the usual laboratory method,¹¹ by passing a current of air through concd. ammonium hydroxide, then through a silica tube filled with copper spirals heated to 400–500°, then through a large quantity of dil. sulfuric acid, followed by passing through another silica tube containing copper spirals and copper oxide heated to 400–500°. The nitrogen was then passed through alkaline pyrogallate solution to remove the last traces of oxygen, through a tower containing silver nitrate solution to remove any sulfur

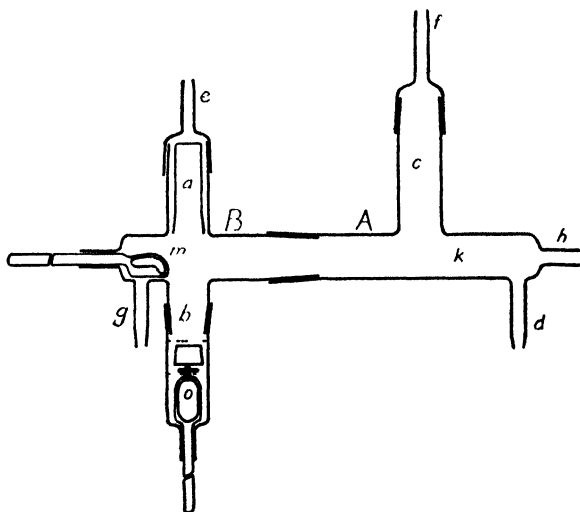


Fig 1

compounds and finally through two towers containing concd. sulfuric acid, two soda lime towers filled with fused potassium hydroxide and then through two long tubes containing phosphorus pentoxide. The dried nitrogen was passed through the quartz and Pyrex bottling apparatus for six hours, heating the whole apparatus to remove any traces of moisture. The stopcocks in the inlet tubes e and g were then closed and the nitrogen was by-passed through a flask containing pure, anhydrous carbon tetrachloride. The carbon tetrachloride was heated to a temperature of 50–60° and the nitrogen bubbled through it. The stream of nitrogen and carbon tetrachloride vapors was passed over the scandium oxide which was heated to about 700°. The temperature was increased to about 850° towards the end so that just a little scandium chloride sublimed from the boat to the top of the tube above the boat. Within

¹¹ Richards and Krepelka, *THIS JOURNAL*, **42**, 2221 (1920).

an hour 1.5 g. of scandium oxide could be completely converted to chloride. The complete conversion to chloride could be attained in a much shorter time by using more carbon tetrachloride and a higher temperature. At higher temperatures ($900-950^{\circ}$), however, it was found that considerable carbon tetrachloride was decomposed and carbon deposited in the quartz tube and on the scandium chloride. In order to obviate this, a lower temperature ($750-850^{\circ}$) was used, and the action of carbon tetrachloride on the oxide was continued for an hour, using only a small quantity of carbon tetrachloride. During the formation of the scandium chloride some material sublimed and was carried into the horizontal quartz tube (k) with the nitrogen stream. At the end of an hour the stopcocks in the inlet tubes e and g were opened and the stopcock in the by-pass tube through the carbon tetrachloride flask was closed. Nitrogen was passed through the entire quartz and Pyrex apparatus through the inlet tubes e, f and g, heating the entire apparatus to $150-200^{\circ}$ in order to drive out the last traces of carbon tetrachloride. The horizontal quartz tube k was heated to a high temperature to remove the small quantity of sublimed material which had come over during the formation of the chloride. Before the sublimation of the chloride this part of the quartz tube was clean and free from any sublimate which had come over during the formation of the anhydrous scandium chloride. At the end of two hours all of the carbon tetrachloride and oxidation products had been removed from the system. The stopcocks in the inlet tubes e and g were then closed, only the inlet tube f being open. The anhydrous scandium chloride in the boat in the quartz tube c was then sublimed to the horizontal quartz tube k in a current of dry nitrogen (at a temperature not exceeding $900-950^{\circ}$). Nearly all of the scandium chloride sublimed into the tube k, opposite and within an inch on either side of the tube c. Half an hour was necessary for a complete sublimation of the scandium chloride.

By heating in this manner, a fractional sublimation of the scandium chloride was carried out. The more volatile impurities such as iron and thorium, were removed during the formation of the scandium chloride. Since the temperature of sublimation did not exceed 950° any rare earth impurities would remain behind in the boat. The tube was then allowed to cool in nitrogen and the stream of nitrogen was displaced by a stream of dry air. The air was first passed through an acid permanganate solution, then through a soda lime tower filled with fused potassium hydroxide, a tower of concd. sulfuric acid, and finally through two long tubes filled with glass beads covered with phosphorus pentoxide. During the passage of the air through the system, the anhydrous chloride was transferred from the quartz tube k to the weighing bottle. This was accomplished by means of the two scoops m and o. The anhydrous scandium chloride was picked up with the scoop m and transferred to

the scoop o. Scoop o was then inserted into the weighing bottle and the chloride deposited there. The outlet tubes for the scoop handles were closed by means of a short piece of rubber tubing wired to the scoop handle. In order to facilitate the working of the scoop m, a quartz rod could be inserted at (h), by means of which the scandium chloride could be pushed into the scoop. In only one or two cases was this necessary. After a little experience in manipulating these scoops, the transfer of chloride from one scoop to another could be carried out with very little loss. Some chloride, however, is lost along the quartz tube k. Only the sublimate which collected around the outlet of Tube c was collected and placed in the weighing bottle. Any chloride which had been carried along the tube k was not collected. After passing air through Tube a for two hours, Tube b containing the stopper for the weighing bottle was inverted and the stopper pushed into the weighing bottle. The weighing bottle was then removed from the Pyrex tube and placed in a large desiccator containing phosphorus pentoxide. It was necessary to remove the stopper from the weighing bottle and clean the ground joint free from scandium chloride. After the stopper had been cleaned and inserted tightly into the weighing bottle, it was removed from the desiccator and cleaned with a damp cloth, dried carefully with a lintless cloth and allowed to stand in a desiccator in the balance room overnight. All joints were fused together throughout the system, except the Pyrex to soft glass, or Pyrex to quartz, which were ground joints.

Weighing.—All weighings were made on a Christian Becker balance No. 9 with weights standardized to 0.02 mg. according to the Richards method.¹² All weights were corrected to a vacuum, vacuum corrections being applied as follows.

	Weights	Silver	Scandium chloride	Air
Density	8.3	10.49	2.733	0.001293
Vac. corr. per g.	...	-0.000031	+0.000318

The density of scandium chloride was determined and the value 2.733 was obtained from an average of three determinations. All weighings were made by the method of substitution.

Analysis

After standing overnight in a desiccator in the balance room, the weighing bottle was placed in the balance and, after two hours, was carefully weighed. One hundred and fifty to two hundred cc. of pure, redistilled water was then frozen in a 2-liter Erlenmeyer flask with a tight-fitting ground stopper. A mixture of ammonium nitrate and crushed ice was used as a freezing mixture free from large quantities of chlorides. The stopper of the weighing bottle was then removed and the weighing bottle

¹² Richards, *THIS JOURNAL*, 22, 144 (1900).

and stopper dropped onto the ice. In order to remove the stopper it was necessary to heat gently around the ground joint. The ice was slowly melted and reaction between the anhydrous scandium chloride and water proceeded mildly. After standing for 24 hours, the stopper of the precipitation flask was removed and the solution diluted to about 1 liter. The scandium chloride dissolved in the water to a perfectly clear solution. The weighing bottle and stopper were removed, washing with much water. Silver was weighed out in the form of buttons to within 0.1–0.2 mg. of the exact equivalent, dissolved in pure, redistilled nitric acid in a flask fitted with a Richards bulb tower, diluted so that the silver was less than 0.1 *N*, and added very slowly to the chloride solution with vigorous shaking after all of the silver had been added. The solution was allowed to stand for four to six days, shaking three or four times a day. The solution was then cooled in ice for three to four hours, samples were withdrawn with a pipet and examined in the nephelometer, adding either silver nitrate or potassium chloride solutions until equilibrium was reached. The solution was allowed to stand for three to four weeks to make sure that it was in equilibrium and that no more "soaking out" had taken place. The silver nitrate and potassium chloride solutions were equivalent to 0.6 g. of silver per liter and were added from a calibrated buret. After equilibrium had been verified two or three times over a period of two weeks, 0.3 mg. of silver threw the equilibrium well over to one side. All operations involving silver chloride were carried out in the dark room lighted with a ruby light. The data for one of the analyses are given in full in order to make clear the corrections applied.

TABLE I

Wt. of ScCl_3 in air, g.	1 02924	Wt. of Ag in air	2 19894
Correction for vacuum (d, 2 733)	+0 00032	Correction for vacuum (d., 10 49)	−0 00007
Wt. of ScCl_3 in vacuum, g	1 02956	Wt. of Ag in vacuum	2 19887
		Nephelometric test	+0 00047
		Total amount of Ag in vacuum, g.	2 19934

The atomic weights of chlorine and silver were taken as 35.457 and 107.880, respectively; $\text{ScCl}_3:3\text{Ag} = 0.468120$; atomic weight of scandium, 45.132. The results are summarized in Table II.

The average results obtained using the scandium oxide purified by the ammonium fluoride method gave 45.173; the average of results obtained using the oxide purified by the ammonium tartrate method gave 45.142, which are in fairly close agreement. The average of these two values gave 45.160; although a little higher than Hönigschmid's value, 45.099, this is a fairly close check, considering the previous values for the atomic weight of scandium.

TABLE II

Sample	Analysis	Wt. of ScCl ₃ in vac., g.	Wt. of Ag in vac., g.	Nephelometric test Ag, g.	Wt. of Ag in vac. g. (corr.)	Ratio ScCl ₃ 3Ag	At. wt. of Sc
I	1	0.59311	1.26725	— 0.00036	1.26689	0.46815	45.142
I	2	1.13724	2.43079	— .00289	2.42790	.46838	45.225
I	3	2.14857	4.59452	— .00528	4.58924	.46817	45.149
I	4	1.10970	2.36999	— .00054	2.36945	.46832	45.202
II	5	1.02956	2.19887	+ .00047	2.19934	.46811	45.132
II	6	1.50457	3.21502	— .00016	3.21486	.46801	45.094
II	7	0.90557	1.93452	— .00043	1.93409	.46822	45.161
II	8	1.79432	3.83723	— .00466	3.83257	.46817	45.151
II	9	1.71420	3.66193	— .00110	3.66083	.46826	45.174
Av. for Sample I							45.179
Av. for Sample II							45.142
Av. of all							45.160

The author desires to express his sincere thanks to Dr. Hiram S. Lukens, under whose direction and kindly encouragement this work was carried out.

Summary

1. Anhydrous scandium chloride was prepared by the action of pure anhydrous carbon tetrachloride on scandium oxide.

2. A new type of bottling apparatus is described for filling the weighing bottle with scandium chloride in the presence of dry air.

3. The ratio of pure scandium chloride to pure silver was determined and the average of nine analyses gave 45.160 as the atomic weight of scandium.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 137]

THE THERMAL DECOMPOSITION OF OZONE. III. THE TEMPERATURE COEFFICIENT OF REACTION RATE

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1. Introduction

In two earlier papers,² the authors have presented the results of investigations on the thermal rate of ozone decomposition, which to a considerable extent explain the lack of agreement among the earlier researches in this field. The resulting clarification of the problem, as well as our discovery of certain improvements in technique, including in particular the discovery of a relatively reproducible source of ozone, have led us also to carry out a new investigation of the temperature coefficient of the rate of this decomposition.

¹ National Research Fellow in Chemistry.

² Wulf and Tolman, *THIS JOURNAL*, **49**, (a) 1183, (b) 1202 (1927).

As will be shown in the latter part of this paper, a knowledge of the temperature coefficient for this reaction is of particular interest, since it appears to afford definite evidence against the mechanism of ozone decomposition suggested by Jahn, which has heretofore seemed the most plausible proposal for this reaction.

2. Previous Researches on Temperature Coefficient

Before proceeding to our own experiments, we must first briefly review the results of earlier determinations of temperature coefficient, and to do this it will be most convenient to give the values obtained from previous work for the energy of activation ΔE as calculated from the Arrhenius equation in the original form

$$d \log k_2/dT = \Delta E/RT^2 \quad (1)$$

where k_2 is the specific second-order rate for the decomposition. As will be shown later, the use of an equation of precisely this form is probably not theoretically justifiable for calculating the energy of activation for this reaction, and indeed the choice of the exactly correct form would involve assumptions as to the mechanism of ozone decomposition which cannot now be made with any degree of certainty. Nevertheless, this is the form used by previous investigators in the field and will be satisfactory for the purpose of comparing results. Furthermore, we shall see later that different forms of the equation lead to values for the energy of activation which do not differ greatly.

The first calculation of temperature coefficient was made by Warburg³ from his measurements of the specific second-order rate at 100° and a total pressure of 91.5 cm. and at 126.9° and a total pressure of 98.1 cm., the difference in pressures arising from the use of oxygen at the same concentrations at the two different temperatures. He thus obtained a result which is equivalent to an energy of activation of 26,700 cal.

The next calculations were made by Clement,⁴ who measured the specific rate by the dynamic method at eight different temperatures in the range 100 to 250° and at a total pressure of 72.9 cm. These measurements would furnish an excellent determination of temperature coefficient were it not for the fact that at 100 and 127°, where from other researches we know the specific rate fairly well, Clement's values are much too high. The reason for this disagreement is not clear, but the disagreement leaves some doubt as to whether any conclusions may be drawn from these measurements as to the temperature coefficient of the normal decomposition. As already pointed out in the first of these articles,⁵ the assumptions made regarding the type of gas flow could hardly have been satisfied

³ Warburg, *Ann. Physik*, 9, 1286 (1902).

⁴ Clement, *ibid.*, 14, 341 (1904).

⁵ See Ref. 2a, where a discussion will be found of the conditions of flow necessary for the dynamic method.

in a reaction vessel of the shape Clement used, but it does not appear that this would cause high calculated values for the specific rate. If the explanation lies in the presence of positive catalyst in the ozone, the temperature coefficient of the normal decomposition might indeed be somewhat different. The value of the energy of activation calculated from Clement's measurements is 26,100 cal.

Perman and Greaves,⁶ in their study of ozone decomposition, observed the reaction at five temperatures over the range 40–120°, always at approximately 1 atm. total pressure; however, their results in general are rather discordant. The decomposition did not appear to proceed in agreement with the second order, and the change with temperature of the average values of the specific rate between temperatures of 100 and 120° was quite different than over the other three intervals. They expressed the specific rates in the units, per minute per millimeter pressure of sulfuric acid. Specific rates are, however, usually expressed in units of concentration, and since at constant concentration the pressure is a function of temperature, the specific rates calculated by them will vary with the temperature in a different way than those expressed in units of concentration. We have converted the average values of their specific rates into the units per second per mole per cubic centimeter, although the use of an average value in such cases is questionable. The values they find for the specific rate for the interval 100–120° then lead to an energy of activation of 38,300 cal. But for the intervals 80–100°, 60–80° and 40–60° the results are 25,900 cal., 26,400 cal. and 26,600 cal., respectively. It does not appear, therefore, that one may conclude much from these measurements. We are chiefly interested in the measurements at 100° and above, for in this region it seems to be easier to carry out the second-order homogeneous decomposition free from disturbing influences. However, their results over the interval 100–120° are so far removed from those over the other three lower intervals that little weight can be given to them.

Belton, Griffith and McKeown⁷ have recently measured the decomposition at 78.1 and 100° and at three different pressures. They give apparently one determination at each pressure of the specific rate at 78.1 and 100°, thus permitting three calculations of the energy of activation. The average of the three values obtained is 27,770 cal. One regrets that the complete data of a typical run are not given, in order to illustrate the extent to which each decomposition adhered to the second order. In earlier work in their Laboratory⁸ it was invariably observed that the decomposition was not of the second order, but that the calculated second-

⁶ Perman and Greaves, *Proc. Roy. Soc.*, **80A**, 353 (1908).

⁷ Belton, Griffith and McKeown, *J. Chem. Soc.*, **129**, 3153 (1926).

⁸ Griffith and McKeown, *ibid.*, **127**, 2086 (1925).

order specific rate increased somewhat over each separate decomposition. It is concluded from what they say that the deviation from second order over each of these decompositions is similar to that observed earlier.

So far as the authors are aware, there are no further measurements in the literature which permit a calculation of the temperature coefficient of this reaction rate. The most reliable previous value of the energy of activation is presumably that of Warburg, of 26,700 cal., our own value, calculated by a method which corresponds to his, has the value of 30,000 cal.

3. Experimental Procedure

In the present work the specific rate of ozone decomposition was measured at five different temperatures, using the dynamic method. The ozone used was the so-called "acid" ozone of our earlier work, which was shown in the second article of this series^{2b} to have very reproducible properties.

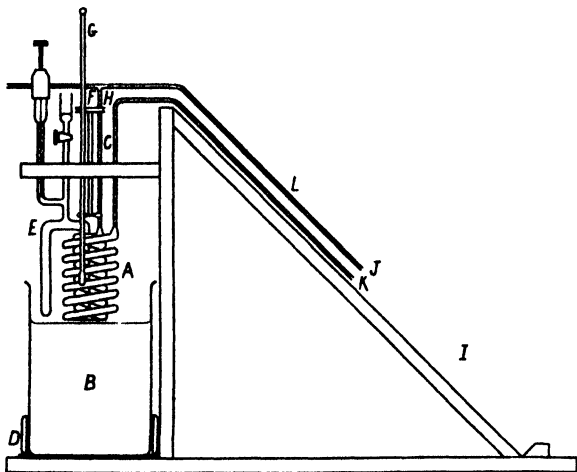


Fig. 1.—Decomposition apparatus.

The ozone was obtained by the electrolysis of sulfuric acid solution at high anode current density and the entire generating apparatus, including the drying train, was the same as that used in our earlier work, with the single exception of a new anode³. The old one had been rendered useless by corrosion eating through the copper cooling pipe within the glass-tube shield. The new unit was identical with the old, except that the glass tube was filled with paraffin up to and around the lead plug anode, thus preventing the electrolyte from entering the glass tube. This protected the copper cooling tube from corrosion.

The decomposition apparatus was new, and the attempt was made to reduce as far as practicable the errors inherent in the dynamic method. The apparatus is illustrated in Fig. 1. The reaction tube A consists of a double concentric helix. This was constructed of Pyrex tubing, approximately 2 meters in length and 5 mm. in bore.

³ For a description of the generating apparatus, see an article by Wulf, to appear soon elsewhere.

The measured volume of this helical reaction chamber was 44.73 cc. The connecting tubes C were of small bore. The helix was suspended in a bath B of paraffin, which was contained in a 3-liter Pyrex beaker and was heated from the outside near its base by a collar heater D. The temperature of the bath was maintained constant by a two-arm mercury regulator E, which controlled through a relay the current in the collar heater. One arm of the regulator was inside the inside coil of the helix and the other arm just outside the outside coil. A motor-driven stirrer F directed the paraffin downward through the helical coils. The thermometer G was placed so that its bulb was close to the outside helical coil and about half way down its depth. All this apparatus was mounted as a unit, independent of the 3-liter beaker, on a cover of hard wood separately supported.

The bath could be raised and lowered, the paraffin never being allowed to solidify over the decomposition apparatus because of the danger of the paraffin crushing the apparatus due to its high coefficient of expansion.

The small-bore connecting tubes of the helical reaction chamber passed upward through the cover. One of these made a T connection at H with the tube line from the ozone-generating set, this line continuing parallel to the other leading-in tube which made a right-angle bend at H, both tubes passing down an inclined surface on which the analytical absorption tubes could be raised or lowered in tracks provided for them.

The apparatus permitted the collection of a sample of gas either at J of the original oxygen-ozone mixture, or at K, this gas having suffered decomposition at the temperature of the bath for the length of time t required to pass through the helical tube. Thus a value of the initial concentration C_0 and of the concentration C after a time t were obtained. These are sufficient data to calculate the specific rate according to the expression

$$k_1 = (1/t) [(1/C) - (1/C_0)] \quad (2)$$

the order being known to be second from our earlier work. A determination of the order was, however, also made at two different temperatures in the present work.

The samples for analysis were collected in absorption tubes especially constructed for the purpose, the method of collection, however, being the same as that previously employed. Fig. 2 shows an absorption tube and the relative amount of potassium iodide solution used. Such a tube in place at I was raised quickly in the trackway over the respective delivery tube to the position L. The orifice of the delivery tube then was roughly 2 cm. above the surface of the absorbing liquid. The volume of gas collected, determined by the rate of flow and the time t_a used in collecting the sample, was considerably smaller than the volume of the tube over the liquid. The sample was thus collected by the upward displacement of the air. After the desired time t_a of collection of the absorption sample, the tube was immediately lowered to the position I, the glass stopper inserted and the tube shaken and set aside, where the absorption was allowed to continue for about an hour. The absorbed sample was analyzed by acidification and titration with standard sodium thiosulfate solution.

During the collection of a sample, the orifice of the other delivery tube was closed by a little distilled water which held itself in place by surface tension. The use of this method of analysis has been described in more detail in the second paper of this series.

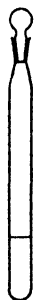


Fig. 2.—
Absorption
tube.

4. Experimental Data

There are three quantities necessary for the calculations of the specific rate at a given temperature, namely: a value of the concentration of the ozone at the reaction temperature and pressure as it enters the re-

action tube; a similar value as it leaves the reaction tube, and the time required for the molecules to make the transit of the reaction tube.

To obtain these it is necessary to measure the following quantities the temperature T , the atmospheric pressure P , which is substantially that in the reaction chamber, the current I in the electrolytic ozone generator, the time t_a used for the absorption of analysis samples, and the titer value of each sample against standard sodium thiosulfate

As an illustration, the complete data for a run made on October 7th are given in Table I. C_0 values, with a few exceptions, were taken one minute after the corresponding C value, many minutes elapsing before the taking of the next C value, since sufficient time must be allowed to set up again the steady-state condition in the helical reaction tube.

TABLE I
DATA OF THE RUN OF OCTOBER 7TH
Pressure, 0.966 atm, t_a , 60 seconds

I amp	T °K	C	Titer cc of thiosulfate	C_0
10 05	452.2	0.88		3.69
10 00	452.2	82		3.66
9 95	441.7	1.42		3.49
10 00	441.7	1.43		3.55
10 00	431.3	2.11		3.45
10 00	431.3	2.10		3.41
9 90	420.9	2.59		3.27
10 00	420.9	2.58 ^a		3.30

^a $I = 9.85$ amp

5. Treatment of the Data

The number of moles of total gas collected in the sample for analysis is given by

$$N = t_a \frac{I}{4 \times 96,500} \left(1 - \frac{1}{3} \alpha \right) \quad (3)$$

where α is the fraction of the total oxygen in the form of ozone. This will be different for the initial and final concentrations. In this work the initial fraction of the total oxygen in the form of ozone was always of the order of 0.018. The correction term $\frac{1}{3} \alpha$ is thus so small that the error involved in assigning a rough average value to α is negligible. The value $\alpha = 0.009$ will be used in these calculations. Combining the numerical factors, we obtain

$$N = 2.583 \times 10^{-6} t_a I \quad (4)$$

The volume of this quantity of gas at reaction temperature T is

$$V = NRT/P = 2.583 \times 10^{-6} t_a IRT/P, \quad V = 2.120 \times 10^{-4} t_a II/P \quad (5)$$

The number of moles of ozone collected in this sample is evidently

$$N_{O_3} = N \times \text{titer (in cc)}/2000 \quad (6)$$

where N is the normality of the thiosulfate. Hence, the concentration

of the ozone initially and finally at reaction temperature and pressure may be computed by dividing Equation 6 by 5, giving us the expression

$$C_{O_3} = 2.359 (NP/t_r T) (\text{titer}/I) \quad (7)$$

The volume of the helical tube, as previously stated, was 44.73 cc. The small-bore connecting tubes were immersed for a distance roughly 2.5 cm. in the bath. The volume of the length immersed was small and the rate of passage of the gas through this volume was high. This tended to raise the entering ozone rapidly to temperature, and similarly the gas leaving was cooled rapidly as it passed quickly out through the long length of small-bore tubing. In using the dynamic method it is assumed that the ozone is raised immediately to reaction temperature as it enters the reaction helix, remains so as it passes through the helix, and is cooled immediately upon leaving it. The assumption is justified here, since the time of heating and cooling is small compared to the time of passage.

The time of passage through the reaction chamber may be assumed equal to the volume of the chamber divided by the volume rate of flow. The conditions necessary for the justification of this assumption are rather complicated, and as they have been treated in the second paper of this series, a discussion of them will not be repeated here. It is, however, well to repeat again that this assumption is not one which at first sight appears justifiable, and is dependent on such factors as shape of vessel and rate of flow. The present apparatus was designed in such a way that the assumption is justifiable.

The volume rate of flow in the reaction chamber is given by

$$r = (I/4 \times 96,500) \times (82.07 T/P)(1 - 1/3\alpha) \quad (8)$$

in cubic centimeters per second, where α is the average fraction of the total oxygen in the form of ozone in the reaction tube. The initial fraction varies but is of the order of 0.018 in this work. The extent of decomposition varies widely over the runs. However, the correction $1/3\alpha$ is less than 1% in any case. Hence it is sufficiently accurate to use as a constant value of the parenthesis 0.997, corresponding to $\alpha = 0.009$ as the average value in the helical tube.

The time of passage through the reaction chamber is then given by

$$t = \frac{44.73}{\frac{I}{4 \times 96,500} \frac{82.07 T}{P} 0.997} = 2.110 \times 10^5 \frac{P}{IT} \text{ seconds} \quad (9)$$

Since ozone decomposition is a change which proceeds homogeneously at a rate proportional to the square of the ozone concentration under the conditions of our experiments, the specific rate may now be calculated. By substituting into the expression

$$k_2 = (1/t_1)[(1/C_1) - (1/C_0)] \quad (10)$$

where C_0 is the concentration of ozone initially at time $t = 0$ and C_1 is this concentration after the time t_1 , we obtain

$$k_2 = \frac{I_1 T}{2.110 \times 10^5 P} \left(\frac{t_2 I_1 T}{2.359 NP \times \text{titer}_1} - \frac{t_0 I_0 T}{2.359 NP \times \text{titer}_0} \right) = \frac{2.009 \times 10^{-6} I_1 T^2 t_2}{NP^2} \left(\frac{I_1}{\text{titer}_1} - \frac{I_0}{\text{titer}_0} \right) \quad (11)$$

6. Results

Using this expression, the specific rate was calculated for the data of five runs comprising 42 sets of initial and final titer values taken at five different temperatures. The results are given in Table II in the column under the absolute temperature at which they were obtained.

TABLE II

Date	VALUES OF k_2 (CC./MOLE SEC.) $\times 10^{-4}$				
	452.2°	441.7°	431.3°	426.1°	420.9°
Oct. 7	21.98	9.93	4.12	..	1.70
	23.80	10.00	4.18	..	1.70
Oct. 21	21.79	10.13	4.57
	21.63	10.30	4.32
Oct. 26	..	11.01	4.10	..	1.68
	...	10.16	4.38	..	1.86
	1.63
	1.67
Oct. 27	23.75	9.99	4.43	..	1.76
	23.00	9.95	4.59	..	1.77
Oct. 28	23.05	10.03	4.57	..	1.82
	22.52	10.03	4.35	..	1.94
Oct. 29	2.75	..
	2.96	..
	2.69	..
	2.82	..
Av.	22.69	10.15	4.36	2.81	1.75
Av. deviation, %	3.1	2.0	3.4	3.0	4.4

The second-order character of the decomposition in the vicinity of these temperatures, as has been said above, was known from our previous work. Even though this was practically the same ozone as we had earlier found satisfactory, it seemed well to test the order in this case also, particularly because of the new decomposition vessel, in view of the possibility that the conditions of flow in the vessel used in the earlier work might not be the same as in this investigation.

In using the dynamic method the order of a reaction may be determined

TABLE III

RESULTS SHOWING SECOND-ORDER CHARACTER OF THE REACTION

T, °K.	t_1 , seconds	Titers (cc. of thiosulfate)	Titers ₁	$k_2 \times 10^{-4}$, cc./mole sec.
420.9	49.1	3.36	2.66	1.68
	48.9	3.39	2.64	1.86
	98.7	3.07	2.08	1.63
	98.7	3.19	2.10	1.67
426.1	48.5	3.90	2.61	2.75
	48.8	3.84	2.53	2.96
	96.6	3.05	1.74	2.69
	96.6	3.16	1.74	2.82

by changing either the initial concentration or the rate of flow or both. Here the rate of flow was changed, but the initial concentration also varied considerably. The results are contained in Table II, but are retabulated here with the times and titer value observed.

The agreement with the second order is evident.

7. The Temperature Coefficient and the Energy of Activation

Although the thermal decomposition of properly prepared ozone is very closely of the second order, the mechanism cannot necessarily be assumed to be bimolecular with respect to ozone because of the known inhibiting effect of oxygen, and at the present time the correct mechanism of the reaction must be regarded as unknown. This introduces difficulties into the determination of the energy of activation, since the precisely correct method of calculation would have to be determined from a knowledge of the mechanism.

For this reason we have calculated the energy of activation ΔE from each of the four following equations and obtained the results shown below,

$$k_2 = k e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30,900 \text{ cal} \quad (\text{A})$$

$$k_2 = \frac{k}{C_{O_2}} e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30,000 \text{ cal} \quad (\text{B})$$

$$k_2 = k T^{\frac{1}{2}} e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30,400 \text{ cal} \quad (\text{C})$$

$$k_2 = \frac{k}{C_{O_2}} T^{\frac{1}{2}} e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 29,600 \text{ cal} \quad (\text{D})$$

k being, of course, a different constant in the four expressions. The different values of ΔE differ from each other by an amount which is somewhat greater than that corresponding to the limit of accuracy in the data.

Each of the above equations would correspond to a different set of assumptions as to the nature of the mechanism responsible for ozone decomposition, although these assumptions would not necessarily be very plausible ones.

Case A is chiefly of interest as giving the simplest empirical expression for the rate of decomposition of dilute ozonized oxygen at 1 atm. total pressure and different temperatures. In order for it to correspond to an actual mechanism we should have to assume that the temperature coefficient of the rate was determined by some unimolecular process with an energy of activation ΔE , and either to neglect the inhibiting effect of oxygen or to assume this inhibiting effect to be determined solely by the total pressure, since this was not varied in our experiments. The mechanism would also have to include steps, perhaps of a chain-like nature, to make the total reaction second order with respect to ozone.

Case B differs from the above in assuming that the rate is to be taken

as inversely proportional to the concentration of oxygen, C_{O_2} . Its interest lies in the fact that Warburg's experiments were made at constant concentration of oxygen, and hence Case B furnishes the most natural value of ΔE to compare with that obtained by Warburg.

Case C would correspond to a mechanism in which the rate-determining step was bimolecular, and the overall rate determined by the total pressure.

Case D corresponds to a mechanism in which the rate-determining step is bimolecular and the overall rate is inversely proportional to the concentration of oxygen, C_{O_2} . This is a particularly interesting case since, as we shall see, the definite mechanism proposed by Jahn fulfils these conditions.

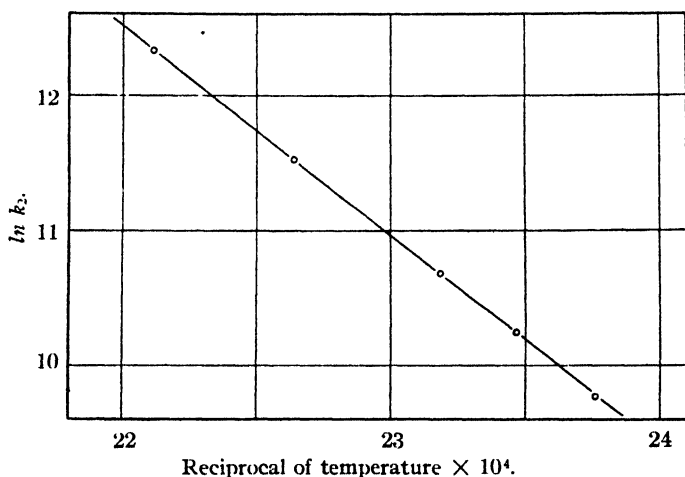


Fig. 3.

These four cases by no means exhaust the possible assumptions as to mechanism. Thus, for example, the inhibiting effect of oxygen might be taken proportional to the number of collisions made between oxygen molecules and some molecular form present during the decomposition rather than to the pressure or concentration. Nevertheless, the four cases show that different assumptions probably will not lead to greatly different values for ΔE .

Let us now turn to a more specific consideration of Case A which gives a simple empirical formula for the rates found, and Case D which corresponds to the Jahn mechanism.

8. Empirical Equation for Rate of Decomposition of Ozone at 1 Atm. Total Pressure

The values of ΔE and k in Expression A were actually obtained by plotting $\log k_2$ against $1/T$ and determining the slope and intercept of the line. The plot of the data given in Table II is shown in Fig. 3. It will

be noticed that the points do fall practically on a straight line, indicating that ΔE may be taken as a constant over the range of temperatures employed.

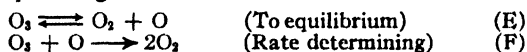
As a result of the plot we obtain as an expression for the specific second-order rate of decomposition of dilute ozonized oxygen at approximately one atmosphere pressure

$$k_2 = 2.04 \times 10^{10} e^{-30,900/RT} \quad (12)$$

This may be regarded as a simple empirical expression for the rate of decomposition of ozone at 1 atm. pressure. At 100° it gives a value of the specific rate of 1.55×10^2 cc. moles $^{-1}$ sec. $^{-1}$. This falls well within the range of values given in the first article of this series for ozone at 100° .

9. The Jahn Mechanism

To explain the inhibiting effect of oxygen and the second-order character of ozone decomposition, Jahn¹⁰ assumed the following intermediate reactions as expressing the mechanism of the overall change.



In accordance with the first of these reactions, we should have for the concentration of monatomic oxygen

$$C_{\text{O}} = K C_{\text{O}_3} / C_{\text{O}_2} \quad (13)$$

where K is the equilibrium constant for the reaction, and hence, in accordance with the second reaction, we could write for the overall rate

$$-dC_{\text{O}_3}/dt = k'T^{\frac{1}{2}} C_{\text{O}_3} K C_{\text{O}_3} / C_{\text{O}_2} = k'KT^{\frac{1}{2}} C_{\text{O}_3}^2 / C_{\text{O}_2} \quad (14)$$

where k' is a constant independent of temperature, and the number of collisions between ozone molecules and oxygen atoms is taken proportional to the square root of the absolute temperature. The mechanism evidently accounts both for the inhibiting effect of oxygen and the second-order character with respect to ozone.

To obtain the effect of temperature on the overall rate, we may now use the van't Hoff expression for the change in equilibrium constant K with the temperature

$$d \log K / dT = \Delta E / RT^2 \quad (15)$$

and by integrating on the assumption that ΔE is constant, and substituting in Equation 14 obtain the result

$$-dC_{\text{O}_3}/dt = kT^{\frac{1}{2}} e^{-\Delta E/RT} C_{\text{O}_3}^2 / C_{\text{O}_2}$$

or

$$k_2 = (k/C_{\text{O}_2}) T^{\frac{1}{2}} e^{-\Delta E/RT} \quad (16)$$

where k is a new constant independent of the temperature and ΔE is evidently the heat absorbed when Reaction E takes place at constant volume.

¹⁰ Jahn, *Z. anorg. Chem.*, **48**, 260 (1905).

It will be noted that Equation 16 agrees with Case D considered above. To determine the values of the constants occurring in Equation 16, we have plotted in Fig. 4 the value of $(\log k - \frac{1}{2} \log T + \log C_{O_2})$ against $1/T$ and thus obtained the numerical equation

$$k_2 = (5.89 \times 10^{13}/C_{O_2}) T^{\frac{1}{2}} e^{-29,600/RT} \quad (17)$$

As will be seen from Fig. 4, the experimental values fall well on a straight line, and in passing it may be remarked that this was also true for the plots corresponding to Cases B and C, which it did not seem worth while to reproduce here. It should also be remarked that if we regard Equation 17 as an empirical expression of the rate of ozone decomposition, it would presumably take reasonable care of the inhibiting effect of oxygen, which is not done by Equation 12.

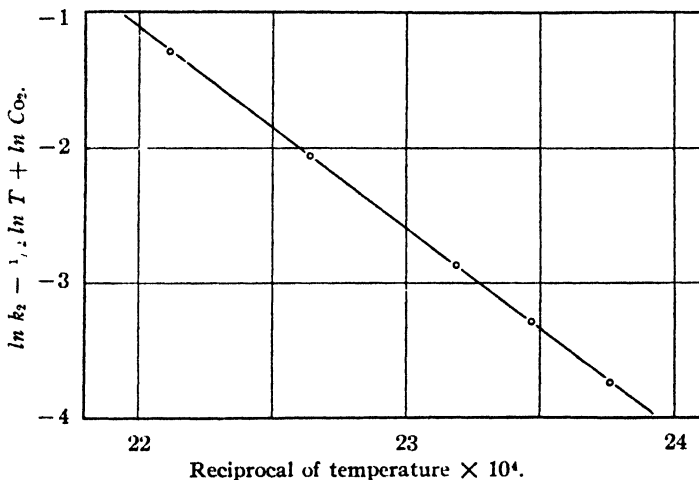


Fig. 4.

10. Energy of Activation on Basis of Jahn Mechanism

Since the Jahn mechanism furnishes us with a definite interpretation of the numerical quantities occurring in Equation 17, we now have the possibility of testing this mechanism by investigating the reasonableness of these quantities.

On the basis of the Jahn mechanism the energy of activation, 29,600 cal., should be the heat absorbed at constant volume by the reaction $O_3 = O_2 + O$, giving us the thermochemical equation $O_3 = O_2 + O - 29,600$ cal. Neglecting the small effect of temperature on heats of reaction we may now combine this with the known heat of decomposition of ozone¹¹ at constant volume and room temperature as given by the equation $2O_3 = 3O_2 + 69,000$ cal., and obtain for the heat of dissociation of

¹¹ See the critical analysis of Moeller, "Das Ozon," Vieweg, Braunschweig, 1921, p. 34.

oxygen at constant volume, $O_2 = 20 - 128,200$ cal., which falls within the probable limits for this reaction.¹²

Hence we must conclude that the Jahn mechanism gives a reasonable value for the heat of dissociation of ozone into diatomic and monatomic oxygen and may use the value 29,600 cal. for our further interpretation.

11. Number of Collisions on Basis of Jahn Mechanism

Turning now to the other numerical factor, namely, 5.89×10^{13} , occurring in Equation 17, it is evident on the basis of the Jahn mechanism that this must be related to the number of collisions between ozone molecules and oxygen atoms. Indeed, as a necessary requirement, it is evident that we could calculate the maximum possible value of this constant by assuming reaction at every collision between an ozone molecule and an oxygen atom. We must now investigate this point.

To do so we shall content ourselves with a comparison of the number of collisions and number of reactions occurring in 5% ozonized oxygen at one atmosphere and 100°. To make this comparison we shall first have to calculate by thermodynamic methods the amount of monatomic oxygen which would be present in 5% ozone at 100°, and then use kinetic theory methods to calculate the number of collisions between monatomic oxygen and ozone.

a. Thermodynamic Calculation of Partial Pressure of Monatomic Oxygen.—To calculate the partial pressure of monatomic oxygen in equilibrium with ozone and molecular oxygen, we must know the heat change ΔH and entropy change ΔS accompanying the reaction $O_3 = O_2 + O$. On the basis of the Jahn mechanism, as we saw above, the energy change accompanying this reaction would be 29,600 cal., and hence the heat change at constant pressure and 100° would be

$$\Delta H_{373} = \Delta E + RT = 29,600 + RT = 30,300 \text{ cal.} \quad (18)$$

To calculate the entropy change accompanying the reaction is more involved. We have, however, at room temperature for the reaction $O_3 = \frac{3}{2}O_2$, the well substantiated value, $\Delta H_{298} = -34,200$ cal., and taking the specific heats of ozone and oxygen as given by the equations¹³

$$O_3, C_p = 7.0 + 0.0071 T - 0.00000186 T^2 \quad (19)$$

and

$$O_2, C_p = 6.50 + 0.0010 T \quad (20)$$

obtain at 0° to the nearest hundred calories the same value

$$\Delta H_{273} = -34,200 \text{ cal.} \quad (21)$$

For the free-energy change at 0°, however, we have the value obtained by Jahn,¹⁴

¹² See Wulf, *THIS JOURNAL*, **47**, 1944 (1925); *Lockrow, Astrophys. J.*, **43**, 205 (1926). See also, however, Hogness and Lunn, *Phys. Rev.*, **27**, 732 (1926). Birge and Sponer, *ibid.*, **28**, 259 (1926).

¹³ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 80, 475.

¹⁴ Jahn, *Z. anorg. Chem.*, **60**, 332 (1908). See also Ref. 11, p. 57, which also takes this value.

$$\Delta F_{273} = -30,000 \text{ cal.} \quad (22)$$

which Jahn considers to be correct within an error that cannot be greater than 2000 cal., and may be considerably less.

Combining Equations 21 and 22 we obtain for the entropy change at 0° the value

$$\Delta S_{273} = (\Delta H - \Delta F)/T = -15.39 \text{ cal. deg.}^{-1} \quad (23)$$

and by integrating from 0 to 100° we obtain, with the help of Equations 19 and 20 for the entropy change at 100°, the value

$$\begin{aligned} \Delta S_{373} &= \Delta S_{273} + \int_{273}^{373} \left[\frac{3}{2} C_p(O_2) - C_p(O_3) \right] \frac{dT}{T} \\ &= -15.03 \text{ cal. deg.}^{-1} \end{aligned} \quad (24)$$

for the reaction $O_3 = \frac{3}{2}O_2$.

Furthermore, for the reaction $\frac{1}{2}O_2 = O$, we have at 25° the entropy change¹⁵ $\Delta S_{298} = 9.97$, and taking the specific heat of monatomic oxygen as 5.0, we obtain for this reaction at 100°, by an integration similar to that in Equation 24, $\Delta S_{373} = +10.33$ cal. deg.⁻¹.

We may now add the values of the entropy changes at 100° for the reactions $O_3 = \frac{3}{2}O_2$ and $\frac{1}{2}O_2 = O$, and obtain for the reaction $O_3 = O_2 + O$, the value $\Delta S_{373} = -4.70$ cal. deg.⁻¹.

Referring back to Equation 18 we may then write for the free-energy change and equilibrium constant for this reaction at 100°

$$-RT \log K_p = \Delta F_{373} = \Delta H_{373} - T \Delta S_{373} = 32,100 \text{ cal.} \quad (25)$$

Solving for the equilibrium constant we obtain

$$K_p = p_{O_2} p_O / p_{O_3} = 1.5 \times 10^{-19} \quad (26)$$

where the partial pressures are in atmospheres. For 5% ozone we obtain for the partial pressure of monatomic oxygen at 100° and 1 atm total pressure

$$p_O = (0.05/0.95) K_p = 7.9 \times 10^{-21} \text{ atm.} \quad (27)$$

This partial pressure corresponds to a very small concentration of monatomic oxygen, of the order, indeed, of considerably less than a molecule per cubic centimeter. Nevertheless, we need have no hesitation on this score in taking the figure as giving the true time average corresponding to the monatomic oxygen present, and using it for calculating the number of collisions between monatomic oxygen and ozone.

b. Calculation of Number of Collisions between Monatomic Oxygen and Ozone.—

The number of collisions between ozone molecules and oxygen atoms per cubic centimeter per second may now be calculated from the kinetic theory expression

$$Z = 1.679 \times 10^{32} C_1 C_2 \sigma_{12}^2 T^{\frac{1}{2}} \sqrt{(M_1 + M_2)/M_1 M_2} \quad (28)$$

where σ_{12} is the sum of the radii of the two different kinds of molecules, and C_1 and C_2 are their concentrations in moles per cubic centimeter. For σ_{12} , which is the sum of the radii of an ozone molecule and an oxygen atom, we shall use the value 3×10^{-8} cm., which is practically the same as Chapman's¹⁶ value 2.93×10^{-8} for the sum of the radii of two oxygen molecules.

Substituting in Equation 28 we obtain

$$\begin{aligned} &1.679 \times 10^{32} \frac{0.05}{82.07 \times 373} \frac{7.9 \times 10^{-21}}{82.07 \times 373} (3 \times 10^{-8})^2 (373)^{\frac{1}{2}} \sqrt{\frac{48 + 16}{48 \times 16}} \\ &= 3.6 \times 10^7 \text{ collisions per cc. per sec.} \end{aligned} \quad (29)$$

Comparison of Number of Collisions and Number of Reactions.—We may now

¹⁵ Ref. 13, p. 464.

¹⁶ Chapman, *Phil. Trans. Roy. Soc.*, **216A**, 347 (1916).

compare this figure with the number of reactions occurring under the same conditions between ozone molecules and oxygen atoms which will be given by the expression

$$Z_{\text{React.}} = \frac{1}{2} k_2 C_{\text{O}_3}^2 N \quad (30)$$

where k_2 is the specific second-order rate at 100° , N is Avogadro's number, and the factor $1/2$ enters because in all, two molecules of ozone are used for each such reaction. Taking the specific rate k_2 at 100° as having the value 1.5×10^2 cc. moles $^{-1}$ sec. $^{-1}$ and substituting in Equation 30 we then obtain

$$\begin{aligned} Z_{\text{React.}} &= \frac{1}{2} \times 1.5 \times 10^2 \times (0.05/82.07 \times 373)^2 \times 6.06 \times 10^{23} \\ &= 1.2 \times 10^{14} \text{ reactions per cc. per sec.} \end{aligned} \quad (31)$$

Comparing Equations 29 and 31, we thus see that the number of collisions would be too small by a factor of more than 10^8 to permit us to account for the decomposition of ozone on the basis of the Jahn mechanism.

To obtain a large enough number of collisions to make the Jahn mechanism possible we should have to assume that reaction between ozone and monatomic oxygen could be induced by an approach of the two molecules to a distance of 5.5×10^{-8} cm., or to assume that the free-energy value in Equation 25 is in error by +11,100 cal.

12. Summary

The temperature coefficient of the thermal decomposition of ozonized oxygen has been measured at one atmosphere's pressure using five temperatures in the range 148 to 179° .

The rate of decomposition may be expressed as a function of the temperature at *one atmosphere* pressure by the empirical equation $-dC/dt = 2.04 \times 10^{20} e^{-30,900/RT} C^2$.

The rate under the same conditions may also be expressed by the equation $-dC/dt = (5.89 \times 10^{13}/C_{\text{O}_3}) T^{1/2} e^{-29,600/RT} C^2$, and this equation will also give reasonable values at total pressures other than one atmosphere.

It has been shown by calculation that the Jahn mechanism of ozone decomposition would require more collisions between ozone molecules and oxygen atoms than could actually occur and hence cannot be regarded as tenable, at least in its original simple form.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 199]

A NEW EQUATION OF STATE FOR FLUIDS.

I. APPLICATION TO GASEOUS ETHYL ETHER AND CARBON DIOXIDE¹

BY JAMES A. BEATTIE AND OSCAR C. BRIDGEMAN²

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PUBLISHED JULY 5, 1927

The consideration of certain thermodynamic properties of fluids has led the authors to formulate jointly an equation of state which appears to reproduce accurately the pressure-volume-temperature data.

It is believed that this equation has to a unique degree the following desirable qualities. (a) The numerical values of the constants can be determined easily and uniquely from the pressure-volume-temperature data, and with one exception can be obtained as the intercepts or slopes of straight lines by suitable treatment of the data. (b) The equation is readily amenable to mathematical manipulation since it is completely algebraic. Hence, most of the usual thermodynamic relations can be integrated in terms of elementary functions as, for example, $p dv$ (and therefore $v dp$) at constant temperature. (c) The equation fits the data over a wide range of pressures and temperatures, reproducing the trends as well as the actual pressures. (d) The volume and temperature functions, A , B and ϵ can be expanded further, *if necessary*, without alteration of the general form of the equation. This extension has not as yet been found necessary in the applications which have been made by the authors to gases even up to pressures of 300 atmospheres.

The proposed equation has the following form

$$p = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2}$$

where $A = A_0(1 - a/v)$, $B = B_0(1 - b/v)$ and $\epsilon = c/vT^2$. This relation is being tested on all of the available data on fluids, and this extensive application, together with a theoretical basis for the equation and the detailed method for obtaining the numerical values of the constants, will be given later.

In the present article, the equation is applied to the data on gaseous ethyl ether³ and carbon dioxide,⁴ and the numerical values of the constants for these substances are given in Table I. The units of pressure, volume and temperature are the atmosphere, cc. per gram, and degrees absolute where $T^\circ = t^\circ + 273.13$.

¹ Originally submitted in two articles under separate authorship.

² National Research Fellow in Chemistry.

³ Beattie, *THIS JOURNAL*, **46**, 342 (1924); **49**, 1123 (1927).

⁴ Amagat, *Ann. chim. phys.*, **29**, 109 (1893). For the method used in interpolating to even volumes, and the values of the pressures so obtained see Bridgeman, *THIS JOURNAL*, **49**, 1130 (1927).

TABLE I

CONSTANTS FOR THE EQUATION FOR GASEOUS ETHYL ETHER AND CARBON DIOXIDE

Constant	R	B_0	b	A_0	a	c
Ethyl ether	1.10777	6.1350	1.6137	5700.0	1.6775	4.5×10^6
Carbon dioxide	1.8650	2.3810	1.6443	2586.0	1.6210	15.0×10^6

The deviations between the observed and calculated values of the pressures for the two gases are presented in Table II.

TABLE II

DEVIATIONS OF PRESSURES CALCULATED BY THE EQUATION OF STATE FROM OBSERVED PRESSURES

(a) Ethyl ether

Temp. °C. Vol., cc./g.	150	175	200	225	250	275	300	325	Average, atm.	Average, press., atm.	Average, dev., %
	$(P_{\text{obs}} - P_{\text{calcd.}}) \times 10^2 \text{ atm.}$										
35	1.7	1.2	2.3	0.5	1.3	-0.6	0.5	1.3	0.012	14.42	0.08
30	3.6	1.9	0.5	1.9	2.5	1.0	1.7	3.1	.020	16.52	.12
25	-1.0	0.2	0.5	1.4	0.2	0.1	2.2	-0.1	.007	19.28	.04
20	-2.2	-0.9	0.0	-0.3	0.4	2.6	0.7	1.7	.011	23.14	.05
15		-3.3	-2.5	-1.6	-0.6	-1.7	0.9	0.1	.015	30.11	.05
12.5		-5.2	-4.1	-3.1	-2.6	-1.6	-2.3	-2.2	.030	34.39	.09
10			-2.3	-2.1	-2.4	-3.3	-5.6	-6.1	.036	42.12	.09
7.5			7.2	6.9	5.5	1.9	1.8	-1.6	.042	50.76	.08
5			-2.5	0.6	-0.2	7.7	5.0	6.4	.037	64.52	.06
									Average	.022	.07

(b) Carbon dioxide

Temp. °C. Vol., cc./g.	0	20	40	60	80	100	Average, atm.	Average, press., atm.	Average, dev., %
	$(P_{\text{obs}} - P_{\text{calcd.}}) \times 10^2 \text{ atm.}$								
40	0	-1	0	-1	-1	0	0.005	14.18	0.04
30	-1	-1	-1	-2	-3	-2	.017	18.53	.09
20	-1	-3	-1	-3	-5	-2	.025	26.69	.09
15	-3	-3	-1	-2	-7	-3	.032	34.17	.09
10		-1	4	3	-6	0	.028	49.73	.06
7		6	15	17	3	7	.096	64.76	.15
5			0	2	-1	0	.008	86.28	.01
							Average	.030	.08

Summary

There is presented a new equation of state which has to a unique extent the desirable features of (a) easy and accurate evaluation of the constants from pressure-volume-temperature data, (b) ease of mathematical manipulation including the integrability of vdp at constant temperature in terms of elementary functions, (c) accurate representation of the data and their trends, and (d) flexibility, in that without alteration of the general form of the equation more terms can be added, if necessary.

The equation, which contains five constants and the gas constant, reproduces the data on gaseous ethyl ether and carbon dioxide at least to a specific volume of 5 cc. per gram, with an average deviation over the whole range of 0.022 and 0.030 atm., respectively (0.07 and 0.08%). An ex-

tensive application to all the available data and a theoretical basis will be given in a later article.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE SOLID SOLUBILITY OF ANTIMONY IN LEAD AS DETERMINED BY CONDUCTIVITY MEASUREMENTS ON COLD-WORKED ALLOYS

BY EARLE E. SCHUMACHER AND GEORGE M. BOUTON

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Introduction

In 1923, Dean¹ showed the existence of an appreciable solid solubility of antimony in lead at the eutectic temperature. Shortly thereafter Dean, Hudson and Fogler² demonstrated that dispersion hardening takes place in these alloys. They found that a 2.5% antimony alloy, a homogeneous solid solution at 247°, precipitated more than half of its antimony from solution after being maintained at room temperature for a short time. A more detailed study of the solubility conditions, using the conductivity method to follow changes of solubility with temperature, was made by Dean, Zickrick and Nix.³ Unfortunately, at the lower temperatures, they were unable to obtain equilibrium values due to the slow rate of precipitation of the solute.

Recent work indicates that the rate of precipitation of the excess of antimony is greatly accelerated if the alloys are first severely cold-worked. Presumably equilibrium would be reached much more quickly under these conditions. Therefore, it seemed desirable to determine the solid solubility values for antimony in lead on severely cold-worked alloys, hoping thereby to secure more accurate values than those previously obtained.

Photomicrographs Showing the Effect of Cold Work

Several photomicrographs, taken by Mr. F. F. Lucas⁴ of these Laboratories, are given to show the structural effect of cold work in these alloys. A lead-antimony alloy containing 1% of antimony and 99% of lead was cast in the form of a rod, 0.5 inch (1.3 cm.) in diameter. This rod was heated at 230° for one hour to get most of the undissolved antimony into solution. The rod was then divided and one section was severely cold-worked by swaging. Both the worked and unworked sections were maintained at room temperature, 20° for five days and then photomicrographs were taken of each. The specimens photographed

¹ Dean, *THIS JOURNAL*, **45**, 1683 (1923).

² Dean, Hudson and Fogler, *Ind. Eng. Chem.*, **17**, 1246 (1925).

³ Dean, Zickrick and Nix, *Trans. Am. Inst. Mining Met. Eng.*, **73**, 505 (1926).

⁴ Lucas, Preprint No. 1654 E, *Am. Inst. Mining Met. Eng.*, February, 1927.

condition before administering the final cold-working. The annealing was followed by a rapid quenching in water, after which the different specimens were severely cold-worked by swaging to approximately 60% of the initial diameter. Samples for chemical analysis were taken just before this final cold-working.

In the case of tests conducted below a temperature of 75°, the wires were immediately placed in a bakelite rack capable of holding 15 specimens. This rack was provided with heavy copper current terminal leads to which the ends of the wires were fastened. The voltage contacts were made of spring brass, sharpened to a knife edge to provide a good contact. When the rack was placed in the thermostat the proper voltage and current connections were made and the test was started. As the test progressed, resistance measurements were made at regular intervals. When the resistance of the wires remained constant for a period of from 200 to 300 hours, equilibrium was considered to have been reached. The wires were then removed from the thermostat and cut off at the knife marks made by the voltage contacts. Their length and weight were accurately determined and their conductivities calculated.

Above 75°, a similar procedure was used except that here the wires had to be protected from direct contact with the oil that filled the thermostat. This was found to be necessary as preliminary tests with several types of oil revealed a development of acidity at temperatures above 75°, which was sufficient to cause corrosion of the test wires. Satisfactory protection was secured by sealing the wires in glass tubes within which the current and voltage contacts were made.

Data typical of those obtained in these measurements are given in Tables I-III. Table I shows the increase in conductivity with time, of some of the wires that were maintained at 25°, and indicates that the conductivity becomes essentially constant before the completion of the test. The data given in Table II were used to prepare the conductivity

TABLE I
SOME CONDUCTIVITY DATA OF LEAD-ANTIMONY ALLOYS
(Conductivity in mhos per cm. cube $\times 10^{-4}$)

Antimony, % Time after swaging, hrs.	0.00	0.22	0.45	0.68	0.99	1.97	3.02
6	4.691	4.582	4.517	4.398	4.241	4.000	3.939
24	4.690	4.582	4.539	4.476	4.263	4.094	4.207
48	4.689	4.580	4.540	4.504	4.293	4.184	4.351
96	4.691	4.581	4.543	4.521	4.346	4.306	4.419
168	4.690	4.583	4.539	4.532	4.399	4.399	4.434
384	4.690	4.583	4.546	4.536	4.482	4.485	4.440
768	4.689	4.583	4.546	4.533	4.528	4.511	4.446
1104	4.690	4.584	4.548	4.533	4.543	4.515	4.447
1512	4.691	4.583	4.546	4.533	4.551	4.518	4.448

TABLE II
CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS AT EQUILIBRIUM
(Mhos per cm. cube $\times 10^{-4}$)

Antimony, %	146°	100°	70°	40°	25°
0.00	3.206	3.648	3.982	4.460	4.691
.10	3.180	3.621	3.963	4.409	4.653
.17	3.174	3.608	3.914	4.385	4.588
.22	3.150	3.596	3.915	4.333	4.583
.34	3.126	...	3.887	4.297	4.549
.45	3.102	3.540	3.861	...	4.547
.56	3.078	3.532	...	4.273	4.540
.68	3.048	3.500	3.841	4.270	4.532
.80	...	3.516	3.858	4.289	4.532
.86	3.042	3.515	3.879	4.281	4.545
.99	...	3.512	3.871	4.267	4.552
1.97	3.007	3.482	3.845	4.250	4.518
3.02	2.954	3.428	3.799	4.203	4.448

TABLE III
SOLID SOLUBILITY OF ANTIMONY IN LEAD

Temp., °C.	146	100	70	40	25
Antimony in soln., %	0.70	0.52	0.48	0.32	0.24

curves at various temperatures. Table III gives the determined values for the solid solubility of antimony in lead at the five different temperatures employed in these experiments.

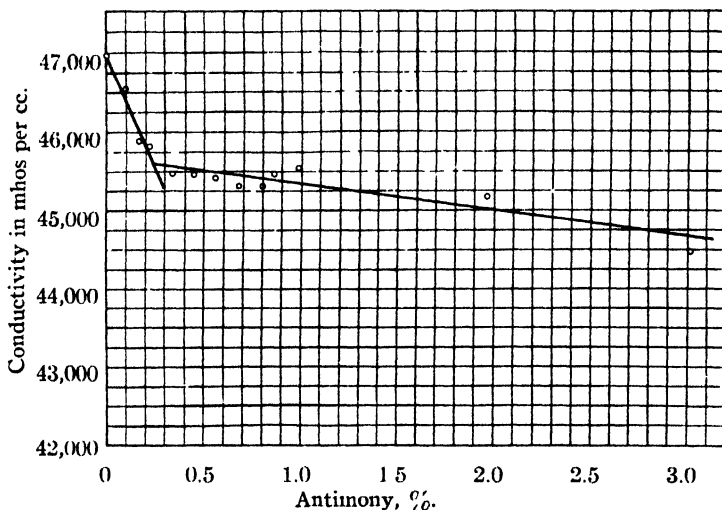


Fig. 4.—Conductivity of lead-antimony alloys at 25°.

Discussion

Since it is evident from the conductivity-time curves, Fig. 9, that at the end of the test the samples were changing very slowly, if at all, we

may assume that the data shown in the conductivity-composition curves, Figs. 4-8, correspond to equilibrium conditions. This assumption is

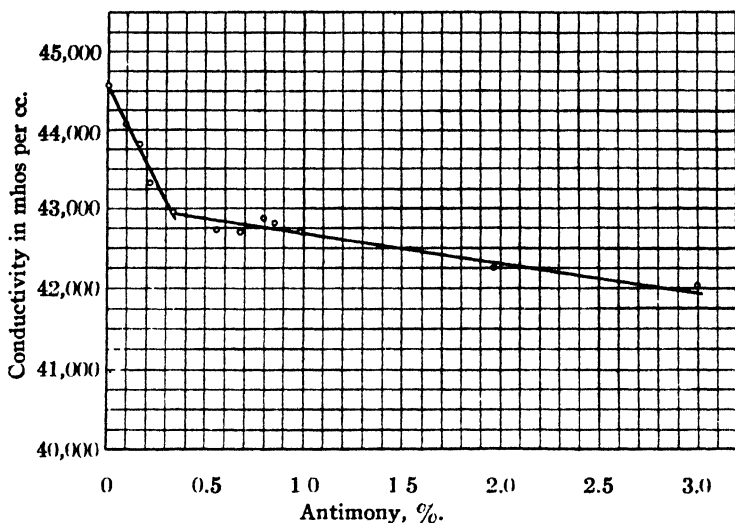


Fig. 5.—Conductivity of lead-antimony alloys at 40°.

also supported by the photomicrographic evidence presented in a preceding paragraph, which showed that shortly after severe cold-working,

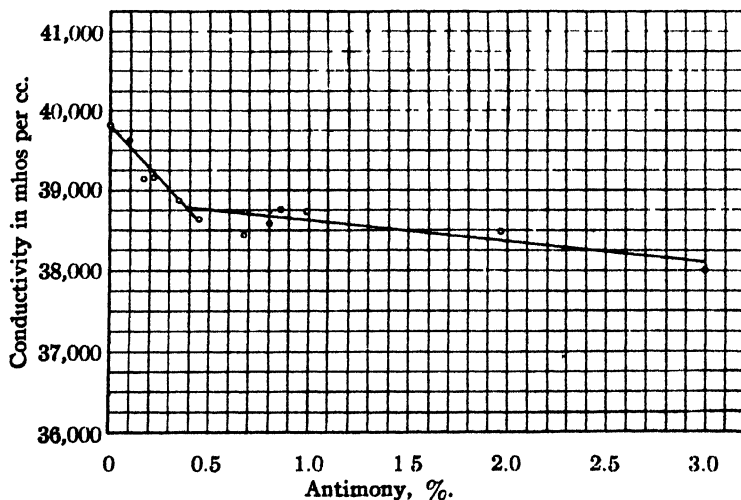


Fig. 6.—Conductivity of lead-antimony alloys at 70°.

samples possess a distribution of antimony similar to that found after prolonged aging in service. These curves accordingly reveal the limiting

values of solid solubility at the respective temperatures. According to the general theory relating conductivity with constitution, alloys lying

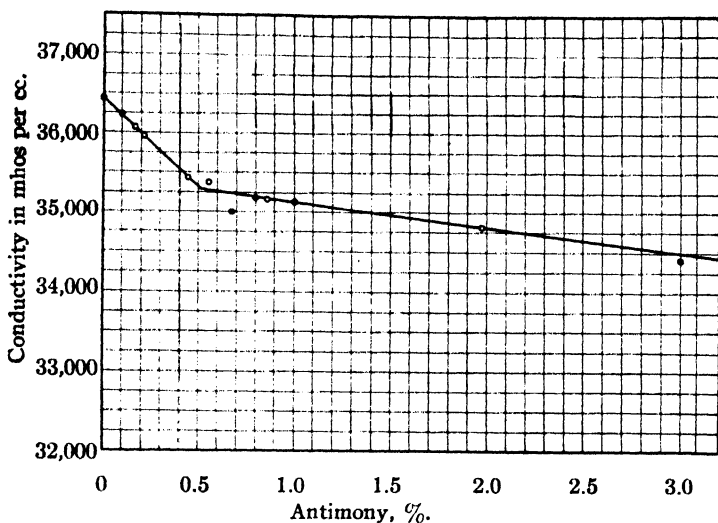


Fig. 7.—Conductivity of lead-antimony alloys at 100°.

within the range of solid solubility should show a rapidly decreasing conductivity with increasing antimony content. Beyond the range of solid

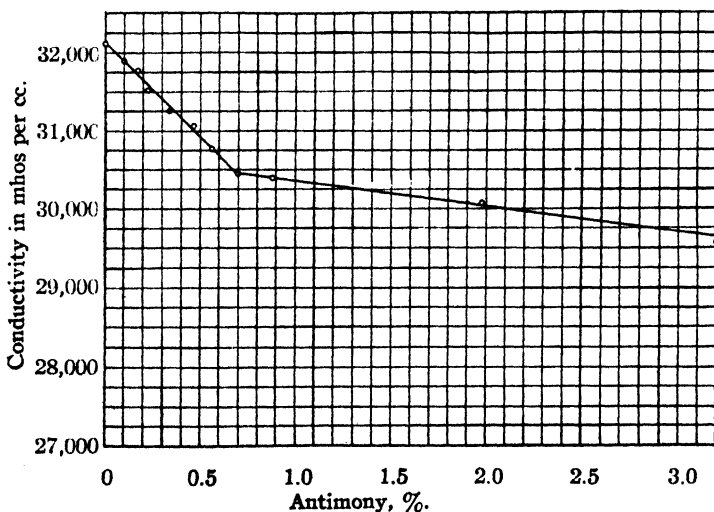


Fig. 8.—Conductivity of lead-antimony alloys at 146°.

solubility the conductivity should change at a much slower rate with increasing antimony content. There should, therefore, be a definite

The Revised Constitutional Diagram for the Lead End of the System Lead-Antimony

Since the liquidus³ and solidus lines⁷ at the lead end of the system lead-antimony have already been accurately determined and we have now contributed precise data defining the change of solid solubility with temperature, it is possible to construct a revised diagram for the lead end of this system. Such a diagram is shown in Fig. 10.⁸

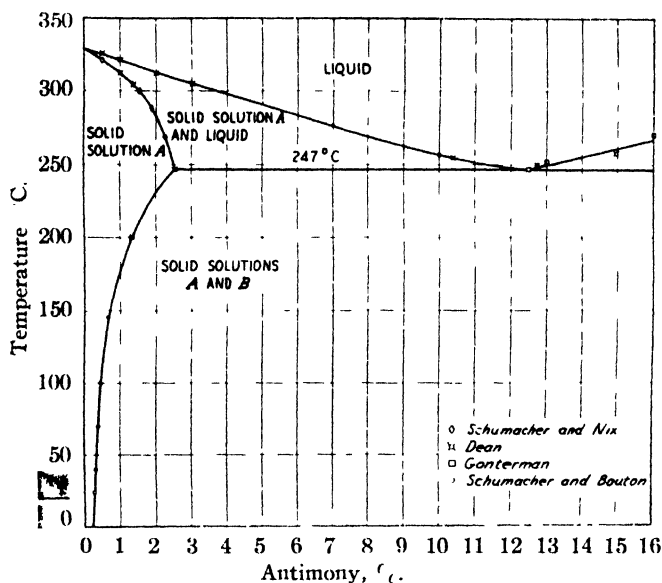


Fig. 10.—Partial equilibrium diagram of the system lead-antimony.

Summary and Conclusions

The solid solubility of antimony in lead has been determined for five different temperatures. The solubility changes from 2.45% at 247°, the eutectic temperature, to about 0.25% at 25°, room temperature. Cold work applied to lead-antimony alloys has been shown to decrease materially the time required to reduce the supersaturation of antimony in lead, and thus permits equilibrium values of the solubility to be more readily obtained. A revised constitutional diagram is given for the lead end of the system lead-antimony.

NEW YORK, N. Y.

³ Schumacher and Nix, Preprint No. 1636 E, *Am. Inst. Mining Met. Eng.*, February, 1927.

⁸ Two points on the liquidus and one on the solidus line were determined during the course of this investigation in order to fix more precisely the location of these lines. The points on the liquidus were determined from cooling-curve data; the point on the solidus was determined by the quenching-test procedure developed by Heycock and Neville.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. II. THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN BENZENE SOLUTION

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Theoretical Part

In the study of the dielectric constants of binary mixtures it has been the custom of most investigators to study the properties of the solutions from curves in which the dielectric constants of the mixtures have been plotted against the mole fractions of the constituents.¹ Following this custom, the results of the first paper of this series² were expressed in that manner. The application of the concept of molar polarization introduced by Debye,³ has marked a distinct advance in the mathematical treatment of the properties of these binary mixtures, particularly in the case where one of the liquids, which may be termed the solvent, is known to have no electric moment. The reasons why this method of treatment is more desirable in the case of these mixtures have recently been discussed in detail by Ebert⁴ and by Debye.⁵

The basis of this method of treatment is found in the familiar Clausius-Mosotti law, $P = [(\epsilon - 1)/(\epsilon + 2)](M/d) = (4\pi/3)N\alpha$, where P is the molar polarization, ϵ the dielectric constant, M the molecular weight, d the density; N Avogadro's number = 6.06×10^{23} and α the molecular polarizability.

The molar polarization, P , has been shown⁵ to be a linear function of the reciprocal of the absolute temperature, so that the equation may be written in the form $P = [(\epsilon - 1)/(\epsilon + 2)](M/d) = (4\pi/3)N[(\mu^2/3kT) + \alpha] = (B/T) + A$, where $B = (4\pi/3)N(\mu^2/3k) =$ effect of orientation of molecules in the field, and $A = (4\pi/3)N\alpha =$ effect due to deformation of molecules. The quantity μ in the above equations is a direct measure of the electric moment of the molecules.

Application to Binary Mixtures.—The molar polarization, $P_{1,2}$, of a binary mixture is given by the expression⁵

$$P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d = f_1P_1 + f_2P_2$$

¹ (a) Linebarger, *Z. physik. Chem.*, **20**, 131 (1896). (b) Philip, *ibid.*, **24**, 18 (1897). (c) Schulze, *Z. Elektrochem.*, **18**, 77 (1912). (d) Kremann, "Die Eigenschaften der binären Flüssigkeitsgemische," F. Enke, Stuttgart, 1916.

² Williams and Krchma, *THIS JOURNAL*, **48**, 1888 (1926).

³ Debye, *Physik. Z.*, **13**, 97 (1912); *Verhandl. deut. physik. Ges.*, **15**, 777 (1913).

⁴ Ebert, *Z. physik. Chem.*, **113**, 1 (1924); **114**, 430 (1924).

⁵ (a) Debye, *Handbuch der Radiologie (Marx)*, **6**, 625 (1925); (b) *Wisconsin Lectures*, Second Semester, 1926-1927.

where f_1 and f_2 = mole fractions of Components 1 and 2; M_1 and M_2 = molecular weights of Components 1 and 2; P_1 and P_2 = molar polarizations of Components 1 and 2; $P_1 = (4\pi/3)N\alpha_1$, and $P_2 = (4\pi/3)N\alpha_2$.

Measurements of the dielectric constants of binary systems in which the first component, the solvent, is known to have no electric moment, permit a calculation of the molar polarization, and therefore of the electric moment of the second component. Liquids such as carbon tetrachloride, carbon disulfide, pentane, hexane and benzene should serve as solvents of this type. The purpose of this paper is to present the results of calculations of the electric moments of certain organic molecules from measurements of the dielectric constants of their solutions in benzene, calculated with the help of the equations given above, and to point out certain limitations to the general application of this method of treatment.

Method

The method used for the determination of the dielectric constants of the binary mixtures was explained in detail in the first paper of this series² and will not be described here. It might be stated, however, that each of two dielectric cells similar to the one described in the previous paper was used for each measurement wherever possible. Since these two cells were of widely different capacitances, the fact that measurements on solutions of the same composition gave the same result within the limit of experimental error would vouch for their accuracy.

The refractive indices of the pure liquids and of the solutions were measured by means of a Pulfrich refractometer immediately after the dielectric-constant determination. Except when noted to the contrary, their densities were determined at 25° by means of an Ostwald-Sprengel pycnometer, taking the usual precautions for temperature regulation.

Purification of Materials

An outline of the method of purification of each substance used is given below. The physical constants of each, density, and refractive index are included as part of Table I, under Experimental Results.

Benzene.—The benzene, obtained from the Eastman Kodak Company, was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide solution and with distilled water. It was frozen out twice and fractionated, and showed no blackening with mercury. The drying agent used was phosphorus pentoxide. The liquid gave practically the same physical constants that are given by Richards and Shipley,⁴ b. p., 80.10–80.15°.

Toluene.—This material was obtained from the Mallinckrodt Chemical Works. It was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide and distilled water. After standing over mercury for a week it was dried with phosphorus pentoxide and fractionated; b. p., 110.60–110.80°.

***o*-Xylene.**—This liquid was obtained from Kahlbaum. It was shaken with concd.

⁴ Richards and Shipley, *THIS JOURNAL*, 41, 2002 (1919).

sulfuric acid, treated with dil. sodium hydroxide solution and washed with water. It was dried with phosphorus pentoxide and fractionated; b. p., 142.3–142.5°.

p-Xylene.—The xylene, also obtained from Kahlbaum, was subjected to a treatment similar to that of the *o*-xylene and fractionated; b. p., 138.3–138.4°.

Chloroform.—The material was obtained from the Eastman Kodak Company. It was treated with concd. sulfuric acid to remove alcohol and washed with dil. sodium hydroxide and water. It was dried over fused calcium chloride. After further drying with anhydrous copper sulfate, it was fractionally distilled; b. p., 61.10–61.20°.

Carbon Tetrachloride.—The preparation (obtained from Merck and Company) was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was then washed with dil. sodium hydroxide solution and water, dried over fused calcium chloride and fractionated; b. p., 76.45–76.52°.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated; b. p., 131.80–131.90°.

Ethyl Ether.—This material was obtained from the Mallinckrodt Chemical Company. It was treated with concd. sulfuric acid, washed, dried with calcium chloride and finally with sodium, and fractionated; b. p., 34.5–34.7°.

Phenol.—The phenol, obtained from Merck and Company, under the label "U. S. P. IX—'C P.'—Loose Crystals," was simply melted and fractionated; b. p., 181.3–181.5°.

Experimental Results

The results of the experimental determinations are summarized in Table I. The columns of this table give, from left to right: the mole fraction of the benzene which was used as the solvent, MFC_6H_6 ; the refractive index of the solution, n_D^{25} ; the density of the solution, d_4^{25} ; the observed dielectric constant, ϵ ; the molar polarization of the solution, $P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d = f_1P_1 + f_2P_2$; and the molar

TABLE I
DIELECTRIC CONSTANT DATA FOR BINARY MIXTURES
GROUP I

1. Benzene— <i>p</i> -xylene					
Mole fraction of C_6H_6 , %	n_D^{25}	d_4^{25}	ϵ	$P_{1,2}$	P_1
100	1.49780	0.8731	2.282	26.73	36.68
50	1.49400	.8612	2.274	31.76	36.68
0	1.49286	.8567	2.265	36.68	36.68
2. Benzene— <i>o</i> -xylene					
100	1.49752	0.8731	2.282	26.73	40.76
90	1.49753	.8727	2.302	28.03	40.76
75	1.49758	.8719	2.337	30.06	40.76
50	1.49766	.8712	2.398	33.57	40.76
0	1.49948	.8704	2.507	40.76	40.76
3. Benzene—phenol ^a					
100	1.49807	0.8728	2.282	26.70	89.0
908924	2.722	32.53	89.0
759242	3.692	41.96	89.0
659447	4.672	48.65	89.0
0	89.0	89.0

TABLE I (Concluded)
 4. Benzene - Carbon tetrachloride^b

Mole fraction of C ₆ H ₆ , %	n_D^{25}	d_4^{25}	ϵ	$P_{1,2}$	P_2
100	1.49780	0.8731	2.282	26.73	28.24
90	1.49738	.9198	2.274	26.83	28.24
75	1.48770	1.0624	2.267	27.09	28.24
50	1.47766	1.2433	2.253	27.46	28.24
25	1.46747	1.4159	2.240	27.85	28.24
0	1.45724	1.5835	2.230	28.24	28.24

5. Benzene - Ethyl ether

100	1.49807	0.8731	2.282	26.73	54.50
75	1.45846	.8297	2.713	33.73	51.50
50	1.42132	.7881	3.183	40.65	54.50
25	1.38496	.7465	3.691	47.52	54.50
0	1.35262	.7077	4.265	54.50	54.50

GROUP 2

Benzene - toluene^{b,c}

100	1.49780	0.8731	2.282	26.73	36.25
91.5	1.49724	.8715	2.304	27.54	34.90
75	1.49649	.8684	2.315	28.60	34.30
50	1.49553	.8651	2.337	30.27	33.84
25	1.49460	.8620	2.362	32.05	33.78
0	1.49392	.8593	2.378	33.66	33.66

7. Benzene - chlorobenzene

100	1.49752	0.8731	2.280	26.73	82.0
90	1.50014	.8993	2.623	31.80	77.4
75	1.50395	.9361	3.131	38.12	74.5
50	1.51012	.9946	3.979	47.71	68.7
0	1.52135	1.1011	5.610	61.81	61.8

8. Benzene - chloroform^c

100	1.49780	0.8731	2.282	26.73	47.5
909292	2.460	28.95	48.9
809844	2.639	30.97	48.0
50	1.47066	1.1590	3.216	36.39	46.0
30	1.2811	3.739	39.83	45.4
0	1.44394	1.4796	4.770	45.00	45.0

¹ Data of Mr. R. J. Allgeier, as yet unpublished. Another article of this series, on the dielectric constants of benzene solutions of certain solid substances, by Mr. Allgeier and the senior author of this paper, will be published in the near future.

^b The dielectric-constant and refractive-index data for these systems were presented in the previous paper of this series.²

^c Density data, d_4^{25} , taken from Linebarger [*J. Am. Chem. J.*, **18**, 429 (1896)] and calculated to d_4^{25} .

polarization of the second component, $P_2 = (P_{1,2} - f_1 P_1)/f_2$, and obtained by graphical methods.

The dielectric constants of the pure liquids and of the solutions were measured at 25°, using a frequency of the order 10^6 cycles per second.

Discussion of Results

Experiments in binary liquid mixtures in which one of the components has no electric moment give results from which certain calculations concerning the electric moment of the other component can be made. The assumption is made in this method of treatment that the polarization due to the non-polar solvent (in this article, benzene) is always directly proportional to its mole fraction in solution. Although for such considerations benzene would appear to be an ideal solvent, and indeed has already been used as such by Lange,⁷ this assumption may not be entirely borne out by experimental data on certain physical properties of the liquids. For example, benzene seems to show a somewhat abnormal behavior in solution with butane.⁸ It shows evidence of a slight association in its specific heat-temperature curve.⁹ It gives a slightly abnormal solution with carbon tetrachloride (a liquid whose moment is without doubt smaller than that of benzene) on the basis of specific-heat relations,¹⁰ etc. It would seem that the assumption, while probably true in an infinitely dilute solution of the second component, fails to take into account what might be termed the chemistry of solution, that is, the changes which take place upon the addition of any finite quantity of the second component. These changes taking place upon solution have been discussed in a number of places,^{10,11} and will not be presented here.

However, for the purpose of discussion, the above assumption will be made in the treatment of the binary mixtures whose constants were presented in Table I. It is convenient to divide the systems into two groups. Group 1 combines the systems in which the molar polarization of the second component, P_2 , is constant throughout the whole range of concentration. These are benzene containing (1) *p*-xylene, (2) *o*-xylene, (3) phenol, (4) carbon tetrachloride, (5) ethyl ether. In Group 2, P_2 is not a constant: benzene containing (6) toluene, (7) chlorobenzene, (8) chloroform.

In Group 1 are found what might be termed ideal solutions, since the molar polarization of the second component is exactly proportional to its mole fraction in the solution. As a typical example of a binary mixture of this type, curves showing the molar polarizations of the second component, and of the solution of benzene and ethyl ether, plotted against the mole fraction of benzene, are presented in Fig. 1. Curve I gives the product of f_1 by P_1 ; Curve II gives the molar polarization of the solution calculated from the relation $P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)](f_1M_1 + f_2M_2)/d$,

⁷ Lange, *Z. Physik*, **33**, 169 (1925).

⁸ Calingaert and Hitchcock, *THIS JOURNAL*, **49**, 750 (1927).

⁹ Williams and Daniels, *ibid.*, **46**, 1569 (1924).

¹⁰ Williams and Daniels, *ibid.*, **47**, 1490 (1925).

¹¹ Hildebrand. "Solubility." Chemical Catalog Co., New York, 1924.

and Curve III gives the molar polarization of ether, P_2 , obtained from Curves I and II. It will be evident from Curve III that P_2 is a constant. This may be interpreted to show that the electric moment of an ether molecule does not change, whether it be completely surrounded by benzene molecules (infinitely dilute solution in benzene), or by both benzene and ether molecules, or by other ether molecules.

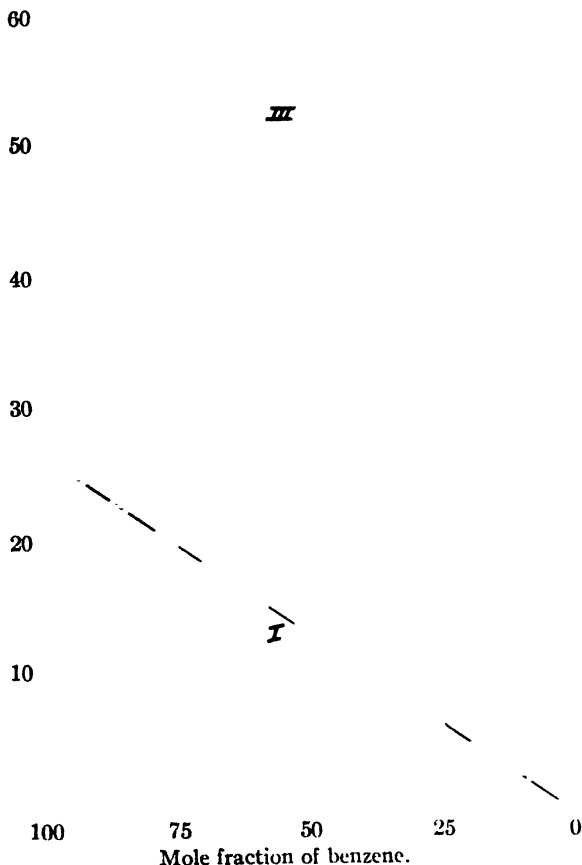


Fig. 1.—Benzene-ethyl ether. Ordinates: Curve I, $f_1 P_1$; Curve II, $P_{1,2}$; Curve III, P_2 .

It should be emphasized that these solutions are ideal only with respect to their molar polarizations in solution. Vapor pressures, specific volumes and specific heats of these solutions may show considerable deviations from ideality, yet their dielectric properties may be normal. The liquids chosen, *o*-xylene, *p*-xylene, phenol, carbon tetrachloride and ethyl ether, represent four different types of organic compounds, only one of which is at all chemically similar to the solvent, benzene.

The binary mixtures in Group 2 give values of $P_{1,2}$ which, when plotted against the mole fraction of the solvent, do not fall on a straight line. Since the molar polarization of the solvent is assumed to be directly proportional to its mole fraction in the solution, it is evident that P_2 will no longer be a constant. These quantities are obtained in a manner exactly analogous to that of the solutions of Group 1.

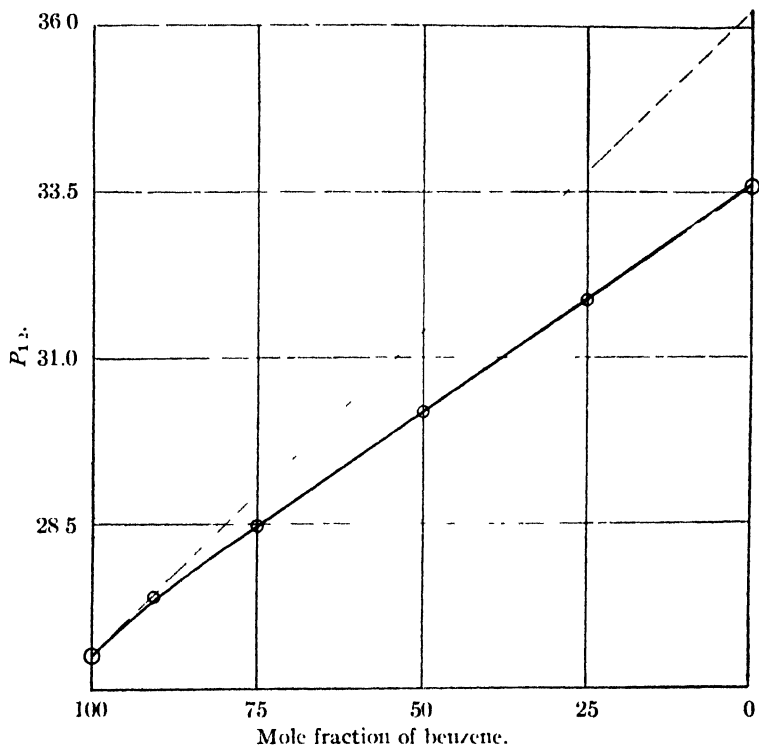


Fig. 2.—Benzene-toluene.

The type of curve obtained for these systems is illustrated by Figs. 2 and 3, in which the molar polarization of benzene-toluene solutions, and the molar polarization of the toluene in solution, respectively, are plotted against the mole fraction of benzene.

In the case of solutions of this group the value of P_2 is obtained by taking a tangent to the $P_{1,2}$ curve at the point where the mole fraction of the reference liquid is unity, and prolonging it until it cuts the axis where the mole fraction of the other component is unity, as shown in Fig. 2. For the intermediate concentrations, the values of P_2 are obtained directly from those of f_2P_2 , since $P_{1,2} = f_1P_1 + f_2P_2$, and $P_{1,2}$ and f_1P_1 are known.

The explanation of the form of curve obtained for systems of this group has been given by Debye.⁵ It is at present a qualitative explanation,

comparable in many respects to the type of explanation given to account for the deviations from ideality of the physical properties of binary mixtures.^{10,11}

Calculation of the Electric Moments of the Molecules

The electric moment of a molecule surrounded by the inert molecules of a non-polar solvent may be calculated in the following manner. The molar polarization of the dissolved substance, P_2 , contains two terms, one a polarization due to orientation, P'_2 , the other a polarization due to deformation, P''_2 , so that the equation $P_2 = P'_2 + P''_2$ may be written. Rearranging, $P'_2 = P_2 - P''_2$. The term P_2 has been calculated for each

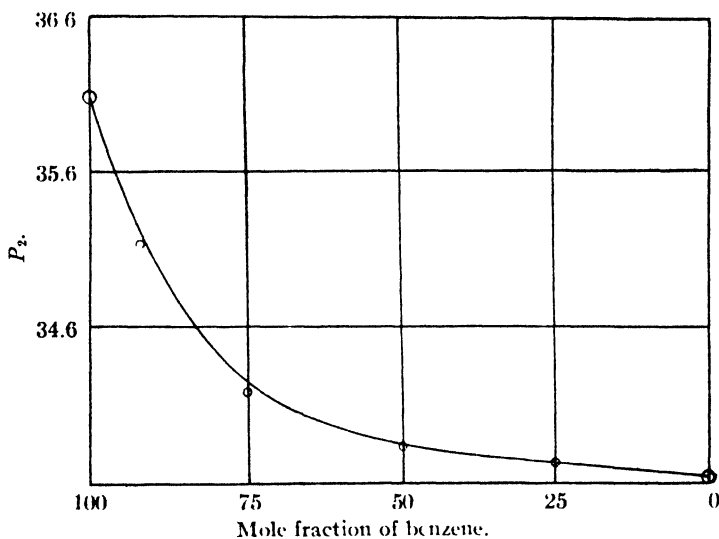


Fig. 3. —Benzene-toluene.

solute in benzene, and included in Table I. For all the calculations of this section the value of P_2 is taken as that value determined in the infinitely dilute solution in benzene, given in the table for 100 mole fraction of benzene. This molar polarization is due, therefore, to a single solute molecule completely surrounded by benzene molecules. The term P''_2 may be approximated by means of the familiar Lorenz-Lorentz¹² formula, $P''_2 = [(N_0^2 - 1)/(N_0^2 + 2)](M/d)$, where N_0 is the refractive index of the substance extrapolated to zero frequency. This extrapolation, of course, can only be made when there is no interfering infra-red absorption. Although it cannot be considered as exact because experimental measurements of the relation between the refractive index and the frequency have not as yet been made in the longer infra-red regions, it gives a result of sufficient accuracy so that the deformation term may be calculated.

¹² Lorentz, *Wied. Ann.*, 9, 641 (1880).

The method of calculation of the electric moment of a molecule is illustrated by a sample computation for the ethyl ether molecule. $P'_2 = P_2 - P''_2 = 54.5 - 23 = 31.5$ cc. $P'_2 = (4\pi/3)N(\mu^2/3kT) = 31.5$, where N is Avogadro's number, μ the electric moment of the molecule, k the Boltzmann constant $= 1.37 \times 10^{-16}$ and T is the absolute temperature, 298° . Making the substitutions, $\mu = 1.22 \times 10^{-18}$.

The electric moments of the several solute molecules, computed in the above manner, are presented in Table II.

TABLE II
ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P''_2 , cc.	P'_2 , cc.	$\mu \times 10^{18}$
Ethyl ether	23.0	31.5	1.22
Carbon tetrachloride	28.3	0	0.00
<i>p</i> -Xylene	35.5	1.0	.06
<i>o</i> -Xylene	35.0	5.8	.52
Chloroform	21.3	26.2	1.10
Toluene	30.3	5.9	0.52
Chlorobenzene	30.2	51.8	1.55
Phenol	27.7	61.3	1.70

Discussion of Table of Electric Moments

Two of the molecules studied, carbon tetrachloride and *p*-xylene, are symmetrical in structure, in which case the electric moment should be zero. The values found indicate that if these molecules have any moment at all it must be of a very small magnitude. Indeed it could hardly be expected that the values of P''_2 might not show an error of ± 1 cc. so that within the limits of the accuracy of the method used, the electric moments of these molecules may be considered to be zero. Since the dielectric constants of benzene and *p*-xylene are so nearly alike, it is difficult to calculate an exact moment for the latter substance in benzene solution.

The electric moments of the toluene and of the *o*-xylene molecule are perhaps somewhat larger than might have been predicted. Smyth¹³ has calculated the electric moments of the toluene and the various xylene molecules "from the indices of refraction at two different wave lengths, the density of the substance under the conditions under which these indices were measured, the dielectric constant at one temperature, the density at this temperature, the value of the temperature itself, the molecular diameter and certain universal constants." These calculated moments are not in particularly good agreement with the experimental ones here presented. The values calculated by Smyth have been criticized by Sanger¹⁴ and will not be discussed here. It is a fact^{2,10} that when small amounts of toluene are dissolved in benzene at 25° , the solution

¹³ Smyth, *THIS JOURNAL*, **46**, 2151 (1924).

¹⁴ Sanger, *Physik. Z.*, **27**, 165 (1926).

behaves abnormally. Since the tangent to the molar polarization curve for an infinitely dilute solution of toluene in benzene gives the quantity P_2 , it must be expected that the term P'_2 will be comparatively large, thereby resulting in a large moment. It is interesting to note that in the case of the symmetrical xylene the electric moment is practically zero, while in the case of the unsymmetrical xylene the electric moment has a significant value.

The values obtained for ethyl ether and chloroform may be compared with others found in the literature. Lange⁷ has determined the electric moment of ethyl ether, obtaining the identical result tabulated above. This investigator determined the dielectric constants of solutions of benzene and ether, using a modified Nernst bridge method. Sanger¹⁵ has recently determined the moment of chloroform in the vapor state with the result $\mu = 0.95 \times 10^{-18}$. The value found in benzene solution is only slightly larger.

Kerr¹⁶ determined the dielectric constants of a number of binary mixtures in which benzene was used as a solvent, among them the system benzene-chlorobenzene. Kerr did not calculate the electric moments of the solute molecules, so that the result given above cannot be compared with others as yet. Indeed, it is the opinion of the present authors that these data are of insufficient accuracy for this calculation, because of the manner of preparing the solutions and of the degree of reproducibility of the dielectric-constant data.

The value reported for phenol would seem to be of the right order of magnitude. It cannot be considered to be exact because certain approximations had to be made concerning the properties of a phenol in the liquid state at the temperature of the measurements.

Conclusion

Although the method of treatment of certain binary systems described above was presented by Debye³ a number of years ago, it is only within recent years that investigators, chiefly chemists, have begun to apply it. This paper and several to follow, using other non-polar liquids as solvents, attempt to show the utility of the Clausius-Mosotti law in the calculation of the electric moments of certain molecules dissolved in a non-polar solvent.

The authors take this opportunity to express their thanks to Professor Debye for his kindly interest, advice and encouragement in the interpretation of the experimental data.

Summary

1. The application of the Clausius-Mosotti law to the treatment of dielectric-constant data of certain binary liquid mixtures has been discussed.

¹⁵ Sanger, *Physik Z.*, **27**, 556 (1926)

¹⁶ Kerr, *J. Chem. Soc.*, **128**, 2796 (1926)

2. The dielectric constants of six binary mixtures at 25° have been determined at various concentrations. The systems studied are benzene-*p*-xylene, benzene-*o*-xylene, benzene-ethyl ether, benzene-chloroform, benzene-chlorobenzene and benzene-phenol.

3. The systems have been grouped for discussion according to whether or not the molar polarization of the solute in solution changes with concentration.

4. The electric moments of each of the solute molecules in benzene solution have been calculated. These results have been critically discussed.

NOTE—Since this paper was written there has appeared an article by Smyth and Morgan [THIS JOURNAL, 49, 1030 (1927)] in which the electric moments of certain substituted benzene molecules were calculated from dielectric-constant and density data. Smyth and Morgan have apparently obtained dielectric-constant and density data for but one system reported in this paper, namely, benzene-chlorobenzene. The data used for the calculations for the moment of phenol were taken from a paper by Philip and Haynes [*J. Chem. Soc.*, 87, 998 (1905)]. Since Smyth and Morgan have withheld their dielectric-constant data for a future publication, and since all the dielectric-constant data used by these authors were obtained using bridge methods rather than one of the newer and more accurate electrical resonance methods, the authors of the present paper have decided to submit their paper in its original form.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL
EXPERIMENT STATION]

ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOAL. IV. THE NON-INVERSION OF SUCROSE BY ADSORBED ACIDS AND ITS SIGNIFICANCE FOR THEORIES OF ADSORPTION AND CATALYSIS¹

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Information that will throw light on the properties and behavior of substances in the adsorbed state is much needed for a better understanding of the nature of adsorption, catalysis, and reactions at interfaces. In the present paper are presented the results of a study of the properties of acids when adsorbed on pure ash-free adsorbent charcoals.

In a previous paper² methods were described whereby adsorbed acids can be removed from pure ash-free charcoal and quantitatively estimated. By means of these methods it was demonstrated³ with hydrochloric acid and pure charcoal that a certain amount of adsorbed acid is held so firmly

¹ Published by permission of the Director of the Experiment Station as Journal Article No. 41.

² Miller, THIS JOURNAL, 46, 1150 (1924).

³ Miller, *ibid.*, 47, 1270 (1925).

that it cannot be removed by washing with water alone, either at room temperature or at boiling temperature. Evidence of the tenacity with which adsorbed acids are held by charcoal is also furnished by the fact that acid is hydrolytically adsorbed from a neutral salt, such as potassium chloride, even in the presence of 0.01 *N* potassium hydroxide and that in order to remove the acid quantitatively it is necessary to extract the charcoal several times by boiling with an amount of alkali somewhat in excess of that equivalent to the acid on the charcoal.

These facts seemed to indicate that the adsorption forces were sufficiently strong to affect profoundly the properties of the acid. They also suggest that the adsorption is not simply a concentration of the acid in the water side of the charcoal-water interface. Further evidence on the properties of adsorbed acids was sought by attempting to determine whether or not adsorbed acids are capable of inverting sucrose and, if so, whether the action is catalyzed by the increased concentration of acid and sugar through adsorption. The ash-free adsorbent charcoals prepared as previously described,⁴ because of their purity and high adsorption capacity, are ideal substances for use in such a study. The amounts of adsorbed acid can be controlled accurately and there can be no doubt that the acids are truly adsorbed and not combined with impurities. The fact that known amounts of acids can be added and quantitatively removed and estimated gives further assurance that the conditions are under strict control.

Materials and Methods Used

The charcoals used in this investigation were from three sources—activated sugar charcoal, Norite and blood charcoal. The method of preparation of the sugar charcoal was essentially the same as that previously described.^{4a} The Norite and blood charcoal were purified by the method described in a previous publication.^{4b} All three charcoals were practically ash-free, containing at the most only a few hundredths of a per cent. of ash. They were all ground to pass through a 300-mesh sieve. The usual tests⁵ for the presence of adsorbed acids and alkaline impurities were applied to each lot of charcoal before use, in order to insure the absence of these substances. The sugar used was recrystallized cane sugar practically free from invert sugar. One g. contained less than a milligram of invert sugar and this was corrected for in blank determinations. The sugar solutions were analyzed for total sugar and invert sugar before and after treatment with the charcoal. Two methods were used: the Shaffer-Hartmann⁶ modification of the Benedict method for the determination of the invert sugar, and Willaman and Davison's⁷ modification of the picric acid method for the determination of both total sugars (sucrose, glucose and fructose) and invert sugar remaining in solution after adsorption.

⁴ (a) Bartell and Miller, *THIS JOURNAL*, **44**, 1866 (1922). (b) Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

⁵ Ref. 4 b, p. 1162.

⁶ Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 375 (1920-1921).

⁷ Willaman and Davison, *J. Agr. Research*, **28**, 479 (1924).

Outline of Procedure

The charcoal (2 g.) was suspended in conductivity water in an Erlenmeyer flask and the system evacuated to remove air and insure thorough wetting. The acid was then added and the suspension allowed to stand with occasional shaking for approximately 16 hours. After this period the charcoal was filtered off with the aid of suction in a Gooch crucible, the filtrate tested for acid, and the charcoal transferred to an Erlenmeyer flask containing 100 cc. of a 5% sugar solution. This suspension was digested with frequent shaking for one and a half hours in a water-bath at 80°. Near the end of the digestion period the charcoal was allowed to settle to the bottom of the flask so that the supernatant solution could be decanted while the temperature was still at 80°. (Since the charcoal suspensions in many cases filtered rather slowly, decantation was necessary in order to keep the suspension from cooling, with the consequent greater adsorption of the solutes at lower temperatures, as would have occurred had the suspension been filtered. Also, by decanting the solution it could be quickly cooled and the inverting action of the acid stopped. While, theoretically, the inversion would go on to some extent in the cold, in practice this action was of negligible magnitude because of the small quantities of acid in the solutions.) The decanted solution was cooled as quickly as possible in running water and then filtered through a disk of filter paper in a Gooch crucible in order to remove the small amount of charcoal that had not settled out. The acid in the filtrate was determined on an aliquot. Since the quantity of acid in the filtrate was usually small, a 50cc. portion was used for titration with 0.02 *N* sodium hydroxide solution. Phenol red was used as indicator. Aliquots of suitable size were taken for use in the methods mentioned above for the determination of total sugar and for invert sugar.

Experimental Part

After a number of preliminary experiments it seemed certain that the only inversion which took place was with the acid and sucrose remaining in solution in equilibrium with adsorbed acids and sugars, for not the slightest trace of invert sugar was ever detected when the charcoal was free from adsorbed acid or when the amount of adsorbed acid was sufficiently small to be adsorbed irreversibly at 80° and was not displaced by the adsorption of sugar at that temperature. It was decided, therefore, to test this point further, using the charcoals with hydrochloric and benzoic acids as representatives, respectively, of groups of acids of low and of high adsorbability. The amount of adsorbed acid held irreversibly adsorbed at 80° depended upon the activity of the charcoal and the adsorbability of the acid. For example, 2 g. of blood charcoal adsorbed irreversibly nearly 10 cc. of 0.02 *N* hydrochloric acid and nearly 50 cc. of the highly adsorbed benzoic acid. When larger quantities of acid were added to the charcoals some acid appeared in solution at 80° in the presence of sugar. In these instances inversion of sugar, of course, always took place. Since relatively large amounts of sugar were also adsorbed, the amount of total sugar (sucrose+invert sugar) remaining in solution at 80° was determined as stated above. The amount of total sugar adsorbed varied with the amount of adsorbed acid on the charcoal. The presence of a large amount of adsorbed acid cut down appreciably the adsorption of the sugar.

It was deemed desirable to determine whether the amount of invert sugar found in the solution after digestion was the same as would be produced by the action of the unadsorbed acid on the unadsorbed sucrose

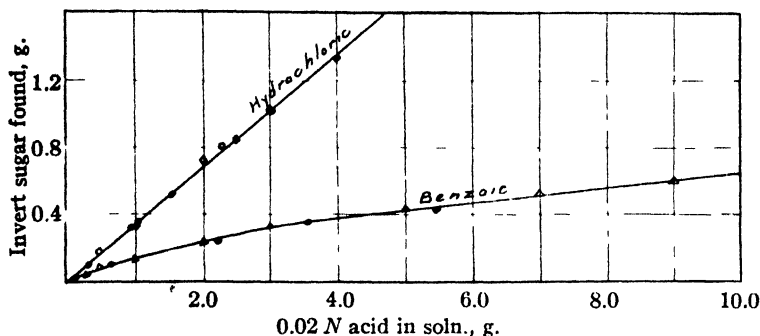


Fig. 1.—Data for blood charcoal. ○, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 3.92% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.35% sucrose.

found in the solution at 80°. If this were found to be the case it would be additional evidence that adsorbed acids are incapable of inverting sucrose. Since it would involve an unnecessarily large amount of work

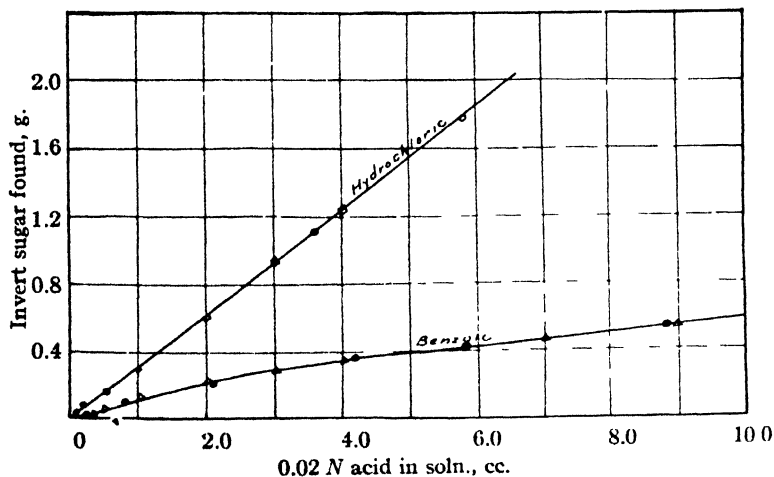


Fig. 2.—Data for Norite. ○, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 4.40% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.64% sucrose.

to determine the amount of inversion by the various amounts of sugar and acid found in solution at 80° and since considerable error might be

introduced in titrating a small quantity of acid (0.1–1.0 cc., 0.02 *N*), a slightly different procedure was followed. The average of the amounts of unadsorbed sucrose found in solution in the experiments with varying amounts of a given acid was calculated. The amount of inversion produced at 80° by given amounts of the acid in question on this amount and concentration of sugar was determined, and from these data a curve was constructed from which could be read the amount of invert sugar that would be produced by the action of any quantity of acid within the range of that found in the solutions in contact with the charcoal in the experiments.

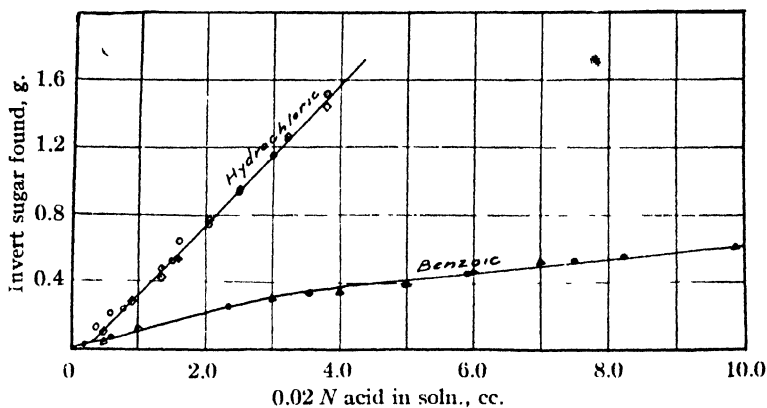


Fig. 3.—Data for activated sugar charcoal. O, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 4.60% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.70% sucrose.

The data for the three charcoals with hydrochloric and benzoic acids and for these acids with the sugar solutions of given concentrations are

TABLE I

DATA FOR PURIFIED BLOOD CHARCOAL AND HYDROCHLORIC ACID

0.02 <i>N</i> acid added to 2 g. of charcoal, cc.	0.02 <i>N</i> acid in soln. at room temp., cc.	0.02 <i>N</i> acid in soln. at 80°, cc.	0.02 <i>N</i> acid on the charcoal at 80°, cc.	Total sugar left in solution at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00		0.00	0.00
2.00	.00	.00	2.00	3.88	.00	.00
5.00	.00	.00	5.00	3.94	.00	.00
7.00	.00	.00	7.00	3.92	.00	.00
10.00	.00	.05	9.95	3.88	.01	.02
12.00	.00	.10	11.90	3.89	.04	.04
14.00	.00	.20	13.80	3.87	.08	.08
16.00	.00	.55	15.45	3.91	.16	.16
25.00	.95	3.60	20.45	4.00	1.10	1.14
30.00	2.00	5.80	22.20	3.99	1.78	1.78

presented in Tables I to XII and in the curves in Figs. 1, 2 and 3. The values are the averages of the results with two or more samples of charcoal.

TABLE II

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 3.92 G. OF SUCROSE AND VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	1.00	2.00	3.00	4.00
Invert sugar in soln. after digestion, g.	0.31	0.61	0.94	1.24

TABLE III

DATA FOR PURIFIED BLOOD CHARCOAL AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in solution at room temp., cc.	0.02 N acid in solution at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	0.00	0.00
10.00	.00	.00	10.00	4.28	.00	.00
49.90	.00	.25	49.65	4.22	.04	.04
74.85	.00	.80	74.05	4.31	.12	.11
99.81	.00	4.15	120.31	4.43	.37	.36
149.72	.45	5.81	143.46	4.34	.43	.43
174.67	.95	8.82	164.90	4.36	.55	.54
199.63	2.00	11.78	185.85	4.36	.65

TABLE IV

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.33 G. OF SUCROSE AND VARYING QUANTITIES OF BENZOIC ACID

0.02 N acid in soln., cc.	0.30	0.50	1.00	2.00	3.00	4.00	7.00	9.00
Invert sugar in soln. after digestion, g.	.04	.08	0.14	0.23	0.29	0.35	0.47	0.55

TABLE V

DATA FOR PURIFIED NORITE AND HYDROCHLORIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	.	0.00	0.00
6.00	.00	.40	5.60	4.38	.12	.06
8.00	.00	.80	7.20	4.39	.22	.22
10.00	.00	1.35	8.65	4.52	.47	.46
12.00	.05	1.60	10.35	4.45	.63	.57
14.00	.20	2.05	11.75	4.42	.75	.76
16.00	.72	2.50	12.78	4.33	.92	.94
18.00	1.35	3.20	13.45	4.42	1.25	1.24
20.00	2.10	3.80	14.10	4.33	1.51	1.48

TABLE VI

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.40 G. OF SUCROSE AND VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	0.50	0.90	1.35	1.50	1.60	2.05	2.50	3.20	3.80
Invert sugar in soln. after digestion, g.	.10	.28	0.46	0.52	0.53	0.76	0.94	1.26	1.44

TABLE VII
DATA FOR PURIFIED NORITE AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	0.00	0.00
50.00	.00	.20	49.80	4.59	.03	.01
74.06	.00	.60	73.46	4.64	.07	.06
100.00	.10	1.98	97.92	4.63	.23	.24
108.63	.60	2.36	105.67	4.60	.27	.26
123.44	.30	3.55	119.59	4.66	.35	.36
133.30	.95	5.90	126.45	4.62	.46	.46
143.17	1.80	7.50	133.82	4.68	.53	.52
148.13	1.85	8.22	138.06	4.68	.55	.55

TABLE VIII
INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.64 G. OF SUCROSE AND
VARYING QUANTITIES OF BENZOIC ACID

0.02 N acid in soln., cc.	1.00	2.00	3.00	4.00	5.00	6.00	7.00	9.88
Invert sugar in soln. after diges- tion, g.	0.13	0.23	0.31	0.35	0.40	0.46	0.50	0.61

TABLE IX
DATA FOR PURIFIED SUGAR CHARCOAL AND HYDROCHLORIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	0.00	00.0
5.00	.00	.35	4.65	4.57	.10	.10
8.00	.00	.93	7.07	4.56	.32	.32
10.00	.10	1.04	8.86	4.62	.36	.36
12.00	.30	1.56	10.14	4.57	.52	.52
14.00	.88	2.28	10.84	4.64	.81	.76
16.00	1.45	3.01	11.54	4.59	1.02	1.01

TABLE X
INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.60 G. OF SUCROSE AND
VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	0.50	1.00	2.00	2.50	3.00	4.00
Invert sugar in soln. after digestion, g.	0.13	0.23	0.31	0.35	0.40	0.46

TABLE XI
DATA FOR PURIFIED SUGAR CHARCOAL AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	0.00	0.00
25.00	.00	.10	24.90	4.70	.01	.01
50.00	.00	.63	49.37	4.68	.10	.09
75.00	.15	2.20	72.65	4.72	.24	.25
85.00	.25	3.56	81.19	4.71	.36	.36
100.00	.40	5.44	94.20	4.67	.43	.44
125.00	1.90	10.89	112.21	4.73	.66

TABLE XII

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.70 G. OF SUCROSE AND VARYING QUANTITIES OF BENZOIC ACID

0.02 <i>N</i> acid in soln., cc.	0.30	0.50	1.00	2.00	3.00	5.00	7.00	9.00
Invert sugar in soln. after digestion, g.	.04	.07	0.10	0.24	0.33	0.44	0.54	0.61

The data show conclusively the following facts. (1) Pure charcoal free from adsorbed acids does not invert sucrose. (2) When the acid is irreversibly adsorbed there is no inversion of sucrose at 80°, even though as much as 1 g. of sucrose was adsorbed by 2 g. of charcoal carrying varying quantities of acids. This would seem to imply a very high concentration of sucrose on the carbon. (3) When sufficient amounts of acid were added to the charcoal so that at 80° there was reversible adsorption and displacement of some of the acid by the sugar, there was always inversion. The amount of sugar inverted under these conditions was the same as that inverted by an amount of acid and sugar equivalent to the unadsorbed acid and sugar under the same conditions but in the absence of charcoal. It is certain that the only inversion is that produced by the acid not adsorbed. (4) Large amounts of adsorbed acid and adsorbed sucrose can be held by the charcoal without producing any inversion at 80°.

Results with Acids of Various Types

In order to determine whether the non-inversion of sucrose by adsorbed acid is a general phenomenon, the behavior of a number of acids of various types was investigated. The procedure was practically the same as above. To 2 g. of blood charcoal was added (1) a quantity of acid sufficiently small so that it was completely and irreversibly adsorbed at 80° in the presence of sugar and (2) a quantity of acid large enough so that at 80° in the presence of sugar some acid appeared in solution. The data appear in Table XIII. The results show conclusively that inorganic, aliphatic,

TABLE XIII

RESULTS WITH ACIDS OF VARIOUS TYPES

0.02 <i>N</i> acid added to 2 g. of blood charcoal, cc.	0.02 <i>N</i> acid in soln. at 80°, cc.	Invert sugar found, g.	0.02 <i>N</i> acid added to 2 g. of blood charcoal, cc.	0.02 <i>N</i> acid in soln. at 80°, cc.	Invert sugar found, g.
5.00 hydrochloric	0.00	0.000	10.00 malic	0.00	0.000
5.00 sulfuric	.00	.000	10.00 tartaric	.00	.000
5.00 nitric	.00	.000	10.00 oxalic	.00	.000
10.00 acetic	.00	.000	39.00 anthranilic	.25	.04
10.00 stearic	.00	.000	40.00 salicylic	.60	.21
10.00 benzoic	.00	.000	20.00 succinic	1.42	.08
10.00 salicylic	.00	.000	20.00 malic	1.62	.17
10.00 anthranilic	.00	.000	20.00 tartaric	1.32	.18
10.00 succinic	.00	.000			

dicarboxylic and aromatic acids, when adsorbed, are incapable of inverting sugar and that inversion takes place only when the adsorbed acids have been displaced from the charcoal.

Results with Salt Solutions and Acid-Salt Mixtures

The data thus far presented show definitely that whatever the mechanism of the adsorption and whatever the condition of the adsorbed acids and sugar on the charcoal, there is no inversion of the sugar by the acid. It has been shown in previous papers^{2,8} that pure ash-free charcoal adsorbs acid hydrolytically from solutions of neutral salts and sets free an equivalent amount of alkali which remains in solution. There is, at the same time, adsorption of some of the solvent, for in the case of the inorganic salts such as potassium chloride, sulfate and nitrate the solution remaining after adsorption is more concentrated with respect to the positive ion than before.³ The inversion or non-inversion of sucrose by the charcoal in salt solutions should yield information regarding the state of the adsorbed acid and adsorbed water. Provided sugar were inverted it would indicate that the acid is free in solution. Non-inversion would show that either or both the acid and sugar and possibly the water, too, are bound in such a manner that they no longer have the properties of ionization and mobility which they possess in ordinary aqueous solution. Since these salt solutions in equilibrium with the adsorbed substances on the charcoal are alkaline, any inversion produced would necessarily have to be attributed to the adsorbed acid on the charcoal or in the film immediately surrounding the charcoal. The procedure in this case was as follows. The charcoal (2 g.) was added to the salt solution or to the acid-salt mixtures and allowed to stand overnight. Sufficient sugar and water were then added to make 100 cc. of a 5% sucrose solution and the

TABLE XIV
RESULTS WITH SALT SOLUTIONS AND ACID-SALT SOLUTIONS

Solution	Activated sugar charcoal		
	0.02 N KOH in soln at 80°, cc.	0.02 N acid on charcoal at 80°, cc.	Invert sugar found, g.
50 cc. 4 N KCl	2.96	2.96	0.000
50 cc. 4 N KCl + 4 cc. 0.02 N HCl	1.87	5.87	.000
50 cc. 4 N KCl + 8 cc. 0.02 N HCl	0.86	8.86	.000
50 cc. 4 N KCl + 12 cc. 0.02 N HCl	0.05	12.05	.000
50 cc. 0.1 N sodium benzoate	9.34	9.34	.000
50 cc. 4 N KCl + 10 cc. 0.02 N H ₂ SO ₄	0.63	10.63	.000
Purified blood charcoal			
50 cc. 4 N KCl	6.95	6.95	.000
50 cc. 4 N KCl + 10 cc. 0.02 N HCl	2.43	12.43	.000
50 cc. 4 N KCl + 20 cc. 0.02 N HCl	0.60	20.60	.000

⁸ Bartell and Miller, *THIS JOURNAL*, **45**, 1106 (1923).

suspension was digested at 80° for one and a half hours as usual. The total quantity of adsorbed acid on the charcoal was the sum of the added acid and the acid hydrolytically adsorbed from the salt solution. The latter was, of course, equivalent to the amount of alkali found in the solution at 80°. The data for sugar charcoal and purified blood charcoal with potassium chloride and sodium benzoate are presented in Table XIV. These data show definitely that there was no inversion under these conditions or even when the quantity of adsorbed acid was augmented by the addition of small quantities of acid to the salt solution. Similar results were obtained when other types of salts, such as methylene blue chloride, were used.

Adsorption of Glucose from Solution

Negative catalysis has sometimes been explained on the theory that the products of reaction are adsorbed so strongly by the catalyst that a coating of the reaction products is formed, through which the reactants cannot diffuse, thereby stopping or slowing down the reaction. The possibility that such conditions might be operative in the present work was investigated. The adsorption of glucose alone and in mixtures with sucrose was determined, as well as the displacement of adsorbed glucose by sucrose. The data in Tables XV and XVI show that the presence of sucrose in the usual 5% solution cut down greatly the adsorption of glucose. It is also evident that the glucose, if formed even in minute quantity on the charcoal, would be largely displaced and would appear in solution where it could be detected. When as little as 5 mg. of glucose was adsorbed on 2 g. of charcoal, more than half of it was displaced when the charcoal was suspended in the usual 100 cc. of 5% sucrose solution at 80°. There is evidence that fructose is even less adsorbed than glucose. It is certain, therefore, that strong adsorption of the products of reaction is not the cause of the negative catalysis in this case.

TABLE XV

ADSORPTION OF GLUCOSE FROM SOLUTION 2 g. of charcoal + 100 cc. of solution at 80°			
Sucrose, g.	Before adsorption Glucose, g.	After adsorption Glucose, g.	Amount adsorbed Glucose, g.
.	4.78	4.30	0.48
5.00	0.99	0.91	.08
5.00	.50	.47	.03

TABLE XVI

DISPLACEMENT OF ADSORBED GLUCOSE BY SUCROSE 2 g. charcoal carrying adsorbed glucose digested with 100 cc. of 5% sugar solution for 1.5 hours at 80°			
Adsorbed glucose, g.	0.020	0.010	0.005
Glucose displaced, g.	.015	.006	.003

Discussion

The results of this investigation show conclusively that acids when adsorbed on charcoal are incapable of inverting sucrose. The fact that the inversion process is not merely slowed up but completely stopped by adsorption is of importance for certain theories of adsorption and contact catalysis.

It seems certain that in adsorption of acids (and probably other substances) from solutions by charcoal there is not merely a concentration of the acid in solution at the interface nor in a highly concentrated film of solution on the adsorbent and separate from the equilibrium solution as postulated by Ostwald and Izaguirre.⁹ If adsorption of acid and sugar were of this nature, inversion undoubtedly would take place.

The results, likewise, point to a conclusion contrary to that frequently accepted with regard to the adsorption of acids. It is frequently considered that when acids are adsorbed there exists at the interface or around the particles of the adsorbent a higher concentration of hydrogen ions than in the bulk of the solution. The existence of a high concentration of hydrogen ions or indeed of any hydrogen ions on the surface of the charcoal particles carrying adsorbed acids seems absolutely disproved by this work. Since it is fairly certain that the inversion of sucrose by acids is due solely to the hydrogen ion it seems reasonable to conclude that the adsorbed acids on charcoal are in an undissociated state.

The possibility that oriented adsorption of either or both the acid or sucrose molecules might be responsible for the negative catalysis seems precluded, in this case at least, by the fact that the reaction is completely inhibited. If it were merely retarded, orientation, whereby there might arise a tendency to keep the reactive parts of the molecules from coming together, would have to be considered. Furthermore, the orientation of the acids would undoubtedly be with the hydrogen ion away from the charcoal and toward, or in, the water phase for it was shown^{8,10} that adsorption by pure charcoal is an oriented adsorption and that the charcoal attracts the hydrocarbon end of the carboxylic acid molecule. The orientation with the carboxyl group and the hydrogen ion toward the water or solution phase should favor inversion, provided, of course, the sucrose molecules were not adversely oriented. According to the "diffuse" double-layer theory of Gouy,¹¹ the hydrogen ions under these conditions should extend for an appreciable distance into the solution. This should result in inversion. The data in Table XIII show, however, that neither adsorbed inorganic acids nor adsorbed carboxylic acids are able to cause inversion. Thus, considerations of orientation also make it seem rea-

⁹ Ostwald and Izaguirre, *Kolloid-Z.*, 30, 279 (1922).

¹⁰ Bartell and Miller, *J. Phys. Chem.*, 28, 992 (1924).

¹¹ Gouy, *J. phys.*, 9, 457 (1910).

sonable to conclude that the adsorbed acid is in an undissociated state.

It is generally considered¹² that charcoal does not catalyze many reactions. There are, however, a number of instances of heterogeneous contact catalysis in which charcoal acts either as a positive or negative catalyst. As illustrations may be cited the work of Firth and Watson¹³ on the catalytic decomposition of hydrogen peroxide and the studies of Kruyt and van Duin¹⁴ on the catalytic effect on the saponification of ethyl acetate, the removal of bromine from α,β -dibromopropionic acid by potassium iodide, and other reactions. The saponification of ethyl acetate was retarded by charcoal while the removal of bromine was accelerated. These authors emphasized the fact that simple adsorption or concentration of the reactants at an interface is not sufficient to catalyze a reaction. They explained the results on the basis of the Langmuir-Harkins theory of oriented adsorption.

Non-inversion of sucrose by adsorbed acids on charcoal is apparently an extreme instance of negative catalysis in which both reactants are adsorbed. As pointed out above, oriented adsorption does not seem to account for the complete inhibition of the reaction. Neither does the theory that the reaction products are so strongly adsorbed that they slow up or stop the reaction seem to offer any possibilities. On the contrary, it appears that the reactants themselves are so strongly adsorbed that they cannot react.

Since the reaction in this instance involves as one of the reactants the hydrogen ion and not the undissociated acid it seems reasonable to conclude that the adsorbed acid on the charcoal is held in the form of undissociated molecules or, possibly, as neutral atoms or groups on the adsorption points of the charcoal lattice. Such an explanation would seem to account satisfactorily for the phenomenon.

Summary

1. Evidence has been submitted to show that adsorbed acids on ash-free charcoals are unable to invert sucrose.
2. It is suggested that adsorbed acids on charcoal are in an undissociated state.
3. Contrary to existing ideas the adsorption of acids does not imply a high concentration of hydrogen ions around the adsorbent.
4. The significance of the non-inversion of sucrose by adsorbed acids for certain theories of adsorption and catalysis has been pointed out.

EAST LANSING, MICHIGAN

¹² Taylor, *J. Phys. Chem.*, **28**, 898 (1924).

¹³ Firth and Watson, *Trans. Faraday Soc.*, **19**, 601 (1924); **20**, 370 (1924-1925).

¹⁴ Kruyt and van Duin, *Rec. trav. chim.*, **40**, 249 (1921).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

THE EFFECT OF INORGANIC SALTS ON THE ADSORPTION OF INORGANIC ACIDS AND BASES

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It is the generally accepted idea that the stability of colloidal dispersions is dependent upon the presence of an electrical charge on the dispersed particle.² This electrical charge is generally conceded to be due to the adsorption of an ion.³ However, the actual mechanism of such adsorption is by no means completely understood. Many investigations have been performed in order to furnish data by means of which some general theory of adsorption could be formulated. Thus far the work done has yielded results which vary widely. Consequently, it has been impossible to formulate any one theory of adsorption which will fit the known facts in all cases. Probably the most important reason for the wide variation in the results published is the use of complex and impure adsorbents. Chemical reactions with impurities would appear as adsorption. Relatively few attempts have been made to purify the adsorbent so that only adsorption would take place.

The investigations on the adsorption of acids and bases by charcoal in the presence of a salt with a common ion, as performed by Michaelis and Rona,⁴ are considered in practically all theoretical discussions pertaining to adsorption. However, Miller's work⁵ has demonstrated that the former investigation is open to criticism. Therefore, for these experiments charcoal was chosen as the adsorbent because it could be prepared in a very pure state.

Some of the experiments of Michaelis and Rona have been repeated, using Merck's blood charcoal as reported by them, as well as a pure form of charcoal.

Preparation and Activation of the Charcoal

Many different methods of purifying charcoal have been published.⁶

¹ A preliminary version of this manuscript was submitted on June 11, 1926.

² Hardy, *J. Physiol.*, **24**, 288 (1899); *Z. physik. Chem.*, **33**, 385 (1900); Zsigmondy and Spear, "Chemistry of Colloids," chap. 3, John Wiley and Sons, Inc., New York, 1917.

³ Nernst, "Theoretische Chemie," Ferdinand Enke, Stuttgart, 1921, p. 367. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 1923. Northrop, Bogue's "Colloidal Behavior," McGraw-Hill Book Co., New York, 1924, p. 77. Burton, *ibid.*, p. 139.

⁴ Michaelis and Rona, *Biochem. Z.*, **94**, 240 (1919); **97**, 268 (1919); **102**, 85 (1920).

⁵ Miller, *THIS JOURNAL*, **44**, 1866 (1922); **45**, 1106 (1923); **46**, 1150 (1924); **47**, 1270 (1925).

⁶ Odén and Andersson, *J. phys. Chem.*, **25**, 311 (1921). Firth and Watson, *J. Chem. Soc.*, **123**, 1750 (1923). Watson, *J. Soc. Chem. Ind.*, **38**, 998 (1919). Herbst, *Biochem. Z.*, **115**, 204 (1921).

Use of commercial charcoals is not satisfactory, since all contain large amounts of impurities. Blood and bone charcoal are known to be of a very complex nature. Even a sample of supposedly pure commercial activated sugar charcoal was found to contain 28% ash. Although the ash from this charcoal was largely soluble in hydrochloric acid, it has been shown that boiling with concentrated acids is inadequate in removing the impurities from the charcoal.⁷ Other suggested methods present similar difficulties. Consequently it was considered necessary to use specially prepared charcoal.

In preparing the charcoal, the best obtainable commercial cane sugar was recrystallized three times from conductivity water. In preparing the conductivity water the same method as that adopted by Harkins was used.⁸ The recrystallized sugar, dried by suction on a Büchner funnel, was then charred at a low temperature in a platinum dish and ignited in order to burn off the adsorbed hydrocarbons.

Another portion of the sugar was charred by treating it with concd. sulfuric acid, and washing until the water showed no acidity when treated with methyl orange.

Freshly charred charcoal is not adsorptive. It must first be activated. Of the various methods suggested for activation, that used by Miller seemed to offer the best source of pure active amorphous carbon. However, steam activation gives a more active carbon, but hydrogen is liberated which is strongly adsorbed and very difficult to remove. For this reason steam activation was avoided except for a few preliminary experiments. Treatment with iodine, sodium carbonate or other reagents presents similar difficulties. Some sugar was charred in platinum dishes, and ground but not passed through a sieve, heated in a quartz tube for 24 hours at about 950° and then activated by steam for 30 minutes. The charcoal was then heated for one hour more in an atmosphere of nitrogen, and allowed to cool under the same conditions. After cooling, the sample was used at once in order to avoid carbon dioxide.

Samples of this produced about the same amount of adsorption of hydrochloric acid and sodium hydroxide. The presence of sodium chloride increased the amount of each adsorbed. Since this is not in agreement with the experiments of Miller, other experiments with alkalis are being conducted and will be given in a later paper. The filtrate from sodium hydroxide solutions was slightly clouded unless a little sodium chloride was added before filtration, in which case a perfectly clear filtrate resulted. The adsorption of pure hydrochloric acid by the steam-activated charcoal was checked by titrating the chlorides according to the method of Volhard. The unactivated charcoals showed no adsorptive power. The results are given in Table I.

⁷ Miller, *Mich. State College Expt Sta Tech Bull*, No. 73, 1926.

⁸ Harkins, *THIS JOURNAL*, 48, 943 (1926).

TABLE I
ADSORPTION BY STEAM-ACTIVATED CHARCOAL

Material used	Concd. NaCl N. F.	0.01 N HCl adsorbed per g. of charcoal per 100 cc. of soln. Titration of acid, cc.	Titration of chlorides, cc.	0.01 N NaOH adsorbed per g. of charcoal per 100 cc. of soln. cc.
Unactivated	0 0	None	None	None
Activated	0	20 20	20.50	18.95
Activated	1 0	27 10		25.90

The charcoal used for the greater part of this work was prepared by heating the sugar which had been charred in platinum dishes to a temperature of 950° in 2×61 cm. quartz tubes for 24 hours. The quartz tubes were enclosed in an asbestos box and heated by five Méker burners. The tubes were packed tightly with charcoal and the ends left open until the maximum temperature was reached. This assisted in driving off any remaining adsorbed hydrocarbons. Then the ends of the tubes were fitted with glazed porcelain stoppers, and so remained until the heating was completed. The final heating was carried out in covered porcelain crucibles in an electric furnace which was kept at 1000° for 48 hours. This charcoal was then ground in an agate mortar to pass through a 200-mesh sieve, and thoroughly mixed. Charcoal prepared in this way is an active adsorbent and contains less than 0.2% of ash. A 10g. sample shaken with conductivity water and allowed to stand for 24 hours and then filtered, left a filtrate which was neutral to the common indicators.

The charcoal which had been charred with sulfuric acid was activated by heating for 24 hours in closed quartz tubes, and for 24 hours more, during which time a measured amount of air was forced through the tube, the amount of air being sufficient to burn about two-thirds of the original charge. This charcoal was also ground in an agate mortar to pass through a 200-mesh sieve. It contained less than 0.05% of ash, and also left a neutral filtrate when shaken with water and filtered.

Procedure

The balance, weights, flask, pipets and burets were calibrated according to the usual methods. Pyrex glassware was used throughout. All solutions were prepared with conductivity water. The acids and bases used were Baker's "Analyzed," and the neutral salts were Merck's "Reagent" products. All of the experiments were performed with 0.0100 *N* acid or base, prepared as follows: 50 cc. of the 0.1000 *N* solution was mixed with a definite amount of salt solution in a 500cc. graduated flask, and diluted to volume. This method gave solutions of the desired neutral salt concentration, which were 0.0100 *N* with respect to the acid or base present. For example, with hydrochloric acid, the acid in each sample was 0.01 *N*, but the concentration of the sodium chloride was increased in successive samples from 0 to 4.5 *N*; 4.5 *N* is the closest normality to the

saturation point with which it is practical to work. Before treating the charcoal these solutions were titrated with 0.01 *N* standard solution, as an assurance that the prepared solutions were exactly 0.0100 *N*.

Phenol red (phenolsulfonephthalein) was the indicator used.⁹ It was prepared from the dye according to Clark's directions.¹⁰ This indicator is extremely sensitive to carbon dioxide; consequently the solutions were all boiled before and during the titration. When dealing with alkaline solutions it was particularly necessary to boil the solutions after each addition of acid in order to determine the true end-point, since during the process of filtration they adsorb carbon dioxide.

From each solution two 125cc. portions were taken. Each portion was shaken with 1.2500 g. of charcoal in a 500cc. Erlenmeyer flask. The flasks were placed in a constant-temperature bath and kept at 25° for 24 hours. This gave ample time for equilibrium to be reached. The charcoal was then removed by filtering. A blank determination showed that the concentration of a solution was unchanged by a possible selective adsorption of the filter paper. Fifty-cc. portions were titrated again, using the 0.01 *N* standard solutions. The difference in the concentrations before and after treatment with charcoal indicated the amount adsorbed. According to this method two 50cc. portions were titrated from each sample and two samples were taken for each salt concentration. This gave four measurements for each result obtained. When unexpected results were obtained, extra samples were prepared and titrated.

Experimental Results

The results for the adsorption of hydrochloric acid are tabulated below

TABLE II

ADSORPTION OF 0.01 *N* HYDROCHLORIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

NaCl, <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution	
	Avg. from each sample	Final av.
0.00	0.0530	0.0515
.10	.0564	.0560
.20	.0744	.0626
.30	.0780	.0780
.50	.0880	.0944
.75	.1078	.1080
1.00	.1158	.1142
1.50	.1254	.1236
2.00	.1386	.1404
2.50	.1444	.1456
3.50	.1702	.1720
4.50	.1925	.1910

⁹ Chesney, *J. Exptl. Med.*, **35**, 181 (1922)

¹⁰ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, p. 80.

in milligram equivalents adsorbed per gram of charcoal per 100 cc. of 0.01 *N* solution. The amount of hydrochloric acid adsorbed increases rapidly with increased concentration of the sodium chloride up to 0.5 to 0.75 *N* concentration of sodium chloride. With more concentrated solutions, in respect to the salt, the increase in adsorption of the acid approaches a linear function of the increase in the salt concentration. This fact is shown graphically in Fig. 1. The milligram equivalents adsorbed are plotted as ordinates, and the concentrations of a salt, expressed in terms of normality, are taken as abscissas.

TABLE III

ADSORPTION OF 0.01 *N* NITRIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM NITRATE

NaNO ₃ , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.1450	0.1480	0.1465
.10	.1830	.1860	.1845
.20	.2052	.2026	.2039
.30	.2094	.2092	.2093
.50	.2202	.2210	.2206
.75	.2334	.2310	.2322
1.00	.2458	.2466	.2462
1.50	.2550	.2598	.2574
2.50	.2912	.2972	.2942
3.50	.3058	.3170	.3124
4.50	.3306	.3336	.3321
5.50	.3670	.3612	.3641

The presence of sodium nitrate affects the adsorption of nitric acid in the same manner. The nitric acid is adsorbed to a greater extent than the hydrochloric acid.

Sulfuric acid in the presence of sodium sulfate exhibits the same general type of curve. However, the amount adsorbed decreases as the amount of sodium sulfate increases. This was contrary to the expected results, and contrary to the results obtained by Michaelis and Rona. Conse-

TABLE IV

ADSORPTION OF 0.01 *N* SULFURIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

Na ₂ SO ₄ , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.0776	0.0810	0.0793
.10	.0608	.0510	.0559
.20	.0272	.0398	.0335
.30	.0252	.0240	.0246
.50	.0170	.0220	.0195
.75	.0142	.0156	.0149
.90	.0140	.0118	.0129
1.00	.0060	.0098	.0079

quently, this work was repeated and the same results were obtained the second time. Also this part of the experiment was repeated with a different type of charcoal, as will be discussed in detail later.

However, the results again showed a decrease in the adsorption of sulfuric acid, upon increasing the concentration of sodium sulfate.

The results of these experiments on the adsorption of acids in the presence of a common ion are shown in graphic form in Fig. 1.

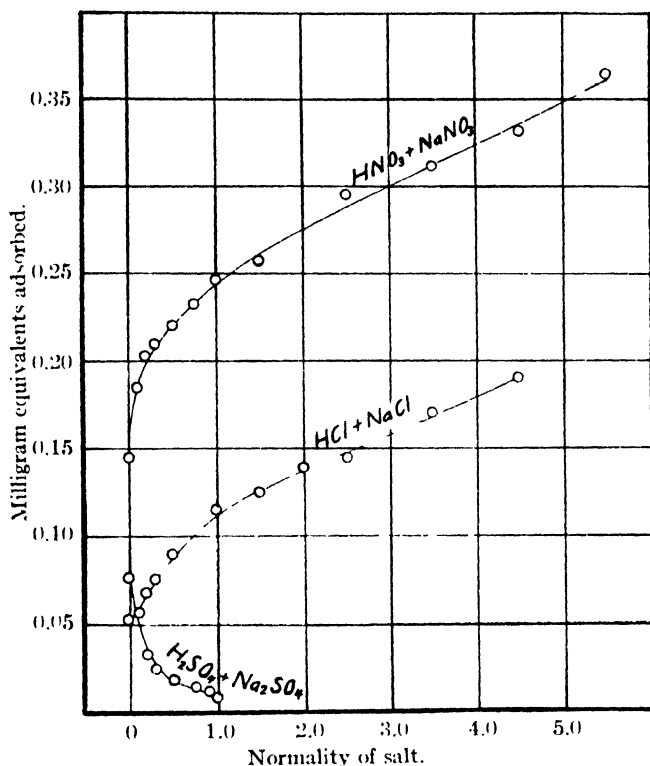


Fig. 1. Adsorption of acids in the presence of a common ion by sugar charcoal - heat charred

In order to show more clearly the difference in the adsorption of the acid further determinations were made. The charcoal prepared by treating with sulfuric acid was used for these determinations. It was more active in adsorbing acids and, therefore, accentuates their differences.

Mixtures of two acids, containing 0.005 *N* solutions in respect to each acid, or of a total acidity of 0.01 *N*, show an adsorption less than that of the more active acid alone, but more than that of the less adsorbed acid. One g. of this charcoal adsorbs from 100 cc. of 0.01 *N* solution 0.1696 mg. equiv. of sulfuric acid, 0.2549 mg. equiv. of hydrochloric acid and 0.3232

TABLE V
ADSORPTION EXPERIMENTS WITH ACID CHARRED CHARCOAL

Original solution	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution Av. from each sample		Final av.
0.01 N H_2SO_4	0.1656	0.1636	0.1646
.01 N HCl	.2552	.2546	.2549
.01 N HNO_3	.3226	.3238	.3232
.01 N NaHSO_4	.1840	.1720	.1780
{ .005 N H_2SO_4	.2950	.2968	.2959
{ .005 N HNO_3	.2530	.2524	.2527
{ .01 N HCl	.5260	.5090	.5175
{ 3.00 N NaNO_3	.5300	.5276	.5288
{ 0.01 N H_2SO_4	.3230	.3156	.3193
{ 3.00 N NaCl	.2236	.2222	.2229

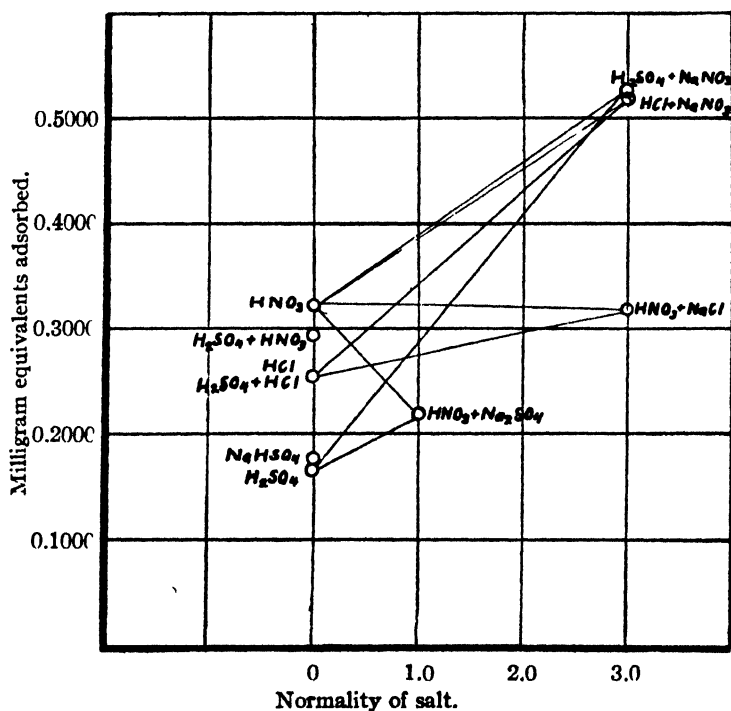


Fig. 2.—Adsorption experiments with mixed acids—sugar charcoal—acid charred.

mg. equiv. of nitric acid. From a mixture of nitric and sulfuric acids, 0.2959 mg. equiv. is adsorbed; from a mixture of sulfuric and hydrochloric acids, 0.2527 mg. equiv. is adsorbed.

Acids in the presence of concentrated solutions of salts without a common ion were also treated, and the amount of adsorption measured. The complete list is tabulated in Table V, and shown in graphic form in Fig. 2.

It was believed that it would be interesting to determine the adsorption of acids and bases in the presence of a common ion, using another type of charcoal. In general the same method was carried out, using Merck's (acid purified) blood charcoal which had been carefully heated to drive off adsorbed gases.

The results are tabulated below, and are shown graphically in Fig. 3.

TABLE VI

ADSORPTION OF 0.01 *N* SULFURIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

Na ₂ SO ₄ , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.2914	0.2976	0.2945
.25	.2790	.2820	.2805
.50	.2696	.2728	.2712
.75	.2664	.2634	.2649
1.00	.2508	.2634	.2571

TABLE VII

ADSORPTION OF 0.01 *N* SODIUM ACID SULFATE IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

Concn. of <i>N</i> Na ₂ SO ₄	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.3490	0.3314	0.3352
.25	.2930	.3012	.2971
.50	.2686	.2760	.2723
.75	.2584	.2654	.2619

TABLE VIII

ADSORPTION OF 0.01 *N* HYDROCHLORIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

NaCl, <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. of each sample		Final av.
0.00	0.2904	0.2864	0.2882
.25	.3200	.3220	.3210
.75	.3560	.3570	.3565
1.00	.3620	.3640	.3630
1.50	.3800	.3810	.3805
2.50	.4065	.4055	.4060
3.50	.4304	.4272	.4288
4.00	.4446	.4460	.4452

TABLE IX

ADSORPTION OF 0.01 *N* SODIUM HYDROXIDE IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

NaCl, <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution Av. from each sample		Final av.
0.00	0.2790	0.2830	0.2810
.10	.3238	.3306	.3272
.25	.3388	.3336	.3352
.75	.3467	.3485	.3476
1.00	.3513	.3560	.3536
1.50	.3640	.3620	.3630
2.50	.3733	.3819	.3776
3.50	.3816	.3824	.3820
4.00	.3818	.3838	.3828

In all cases the same relative amounts were adsorbed, which resulted in similar curves to those for pure sugar charcoal. Hydrochloric acid and sodium hydroxide show an increased adsorption as the concentration of the sodium chloride increases. Sulfuric acid shows a decrease as the concentration of the sodium sulfate increases. Sodium acid sulfate shows a rapid decrease with increased concentration of sodium sulfate.

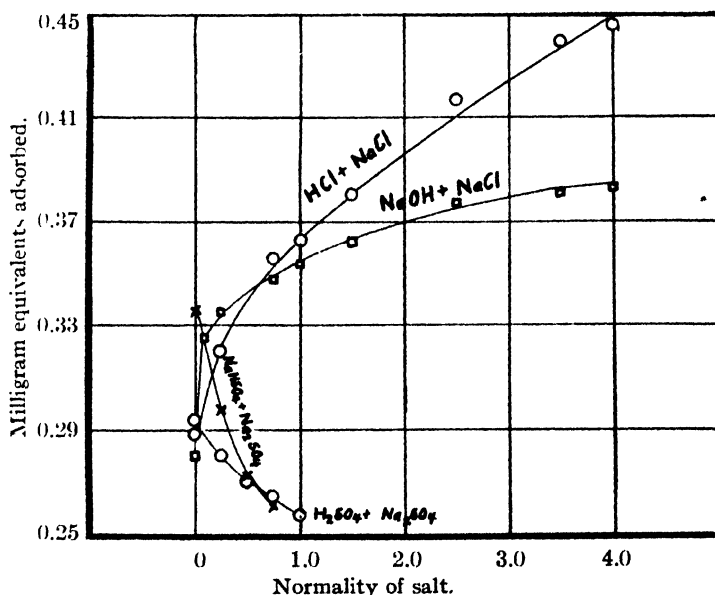


Fig. 3.—Adsorption experiments with blood charcoal.

Discussion and Interpretation of Results

The adsorption of an ion gives a charge to the colloidal particle which attracts to it, although less strongly, the oppositely charged ion of the electrolyte. The resultant effect is a reversible equilibrium of electrostatic

forces. There is the attraction of the colloidal particle for the ion which it adsorbs. Also there is a tendency for the oppositely charged ion to diffuse through the solution, attracting to it the adsorbed ion. The direction of this last attraction is away from the colloidal particle.

The effect of the attraction away from the colloidal particle will depend upon the degree to which the ion is adsorbed. Langmuir's explanation for the adsorption of gases by charcoal¹¹ undoubtedly applies here. "Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom."

There is a stage in adsorption which is approximately irreversible. This has been pointed out by Miller in his description of the difficulty with which part of the adsorbed acid is removed from the charcoal by washing with pure solute. This stage may be pictured as the part of the hydrogen ions which are surrounded on nearly all sides by carbon atoms. Of course if these hydrogen ions cannot be removed by washing, the anions must also remain in the charcoal or in close proximity to it. In the case of hydrochloric acid, for example, when the increased adsorption in the presence of sodium chloride occurs, the same picture is applicable. The excess of chloride ions in the solution decreases the tendency of the chloride ions of the hydrochloric acid to diffuse; consequently, its attraction upon the hydrogen ion away from the particle is lessened. This allows the hydrogen ions adsorbed to become more firmly attached to the carbon, by penetrating further into the spaces between the carbon atoms. This penetration leaves room for more hydrogen ions to be adsorbed, although less firmly, at places nearer the surface of the carbon particle.

In this investigation it was found that 0.01 *N* sodium hydroxide solutions, when filtered, remain cloudy in appearance even after all possible charcoal was filtered out. Evidently the charcoal was peptized by the sodium hydroxide to form a colloidal dispersion. However, when solid sodium chloride was added to this cloudy filtrate, the dispersed charcoal rapidly settled out, and was easily filtered. Evidently the excess of sodium ion decreases the ionization of the sodium hydroxide so that the adsorbed hydroxyl ions are electrically neutralized by the sodium ions, and the colloidal particles are discharged and precipitated. The adsorbed sodium hydroxide remains on the particles when they are precipitated. This is shown by the fact that removing the charcoal decreases the alkalinity of the solution. On this basis the charcoal particles should be dispersed again when the precipitating agent, sodium chloride, is removed by wash-

¹¹ Langmuir, *THIS JOURNAL*, 38, 2286 (1916)

ing, because of the renewed dissociation of the adsorbed sodium hydroxide. This is indeed the case.

There is no evidence discovered in this work for assuming hydrolysis of the neutral salt. There is, rather, evidence that hydrolytic adsorption does not take place. Sodium chloride increases the adsorption of both the hydrochloric acid and sodium hydroxide. Therefore, if it were due to hydrolytic adsorption we should have hydrochloric acid adsorbed preferentially by charcoal in the case of hydrochloric acid and sodium chloride, and sodium hydroxide in the case of sodium hydroxide and sodium chloride, which would be very mysterious indeed.

Since in a saturated solution of sodium chloride it is not possible to suppress entirely the ionization of 0.01 *N* hydrochloric acid, a continual increase in adsorption with increased concentration of sodium chloride is to be expected. Michaelis states that a maximum adsorption is reached when acid-salt mixtures up to 2 *N* with respect to sodium chloride are used. However, up to and including 4.5 *N* solutions with respect to sodium chloride, no evidence of a maximum adsorption of hydrochloric acid was discovered. The work included not only adsorption by sugar charcoal, but also Merck's blood charcoal, as used by Michaelis.¹² Evidently the thermodynamic basis upon which his theory of adsorption rests does not fit the experimental facts.

The adsorption of nitric acid from sodium nitrate solutions is exactly analogous to the case already considered. The fact that nitric acid is more strongly adsorbed than hydrochloric acid shows that although both the nitrate and chloride ions are less strongly attracted to the charcoal than are the hydrogen ions, the nitrate ion is more strongly attracted than the chloride ion.

The decrease in the adsorption of sulfuric acid in the presence of sodium sulfate can be accounted for on the basis of the above theory. The reaction $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{NaHSO}_4$ undoubtedly takes place to some extent. The greater the concentration of the sodium sulfate, the more sodium acid sulfate will be formed. In an excess of sodium sulfate, the sodium acid sulfate will liberate very few free hydrogen ions. Consequently, the higher the concentration of the neutral sulfate, the fewer the hydrogen ions in the solution available for adsorption.

The 0.01 *N* solution of sodium acid sulfate alone is quite noticeably adsorbed. However, when sodium sulfate is added, the decrease in adsorption with increased concentration of added salt is much more rapid than in the case of sulfuric acid. Here again the results obtained are in disagreement with those obtained by Michaelis. His data show an increase in the adsorption of sulfuric acid in the presence of increased concen-

¹² Svedberg, "Colloid Chemistry," Chemical Catalog Co., Inc., New York, 1924, p. 178.

tration of the sulfate ion. Consequently, samples of such mixtures were treated with blood charcoal, as well as with the sugar charcoal, and the decrease in the adsorption was again demonstrated.

Furthermore, dealing with another type of charcoal, that charred with sulfuric acid, it was observed that 1 *N* sodium sulfate decreases the adsorption of nitric acid. One g. of charcoal adsorbed 0.3232 mg. equiv. of nitric acid from 100 cc. of 0.01 *N* solution. With the same acid concentration, containing sodium sulfate, 0.2229 mg. equiv. is adsorbed. Some of the hydrogen ions are tied up with the sodium acid sulfate in the presence of the excess sodium sulfate, according to the reaction $\text{HNO}_3 + \text{Na}_2\text{SO}_4 = \text{NaHSO}_4 + \text{NaNO}_3$. Consequently, there is less adsorption than with nitric acid alone.

When the adsorption from a mixture of 3.0 *N* sodium chloride and 0.01 *N* nitric acid is determined, an amount less than the adsorption of free nitric acid is again shown. This is to be expected because of the reaction $\text{HNO}_3 + \text{NaCl} = \text{HCl} + \text{NaNO}_3$. Hydrochloric acid is less adsorbed than nitric acid, but the adsorption of the hydrochloric acid formed is augmented by the excess sodium chloride present. The amount adsorbed is, therefore, greater than the adsorption of pure 0.01 *N* hydrochloric acid, but slightly less than that of pure 0.01 *N* nitric acid.

Sodium nitrate, 3.0 *N* with 0.01 *N* solutions of either hydrochloric or sulfuric acid give an adsorption greater than that of any of the pure acids. The results are similar to the adsorption of nitric acid in the presence of concentrated solutions of sodium nitrate.

The results of the adsorptions of mixed acids are not surprising, but give further evidence of the relative adsorbability of the acids considered.

Summary

1. The phenomena of adsorption are explained on the basis of the attraction of ions by colloidal particles and the effect of mass action upon this attractive force.
2. It has been demonstrated, as has been generally conceded, that the hydrogen ions of inorganic acids and the hydroxyl ions of inorganic bases are the most strongly adsorbed.
3. The nitrate ion is more strongly adsorbed than the chloride ion, and the chloride ion is more strongly adsorbed than the sulfate ion.
4. Relative results can at any time be duplicated, but it is difficult to obtain separately prepared charcoals with the same degree of activation.
5. There is no evidence of hydrolytic adsorption of neutral inorganic salts in the presence of inorganic acids or bases.
6. There is no maximum adsorption of acids in the presence of a salt with a common ion.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 201, AND FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. VI. FURTHER DEVELOPMENTS IN EXPERIMENTAL TECHNIQUE

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1. Introduction

Many of our experimental methods in the use of the moving boundary for measuring transference numbers have been described in the earlier papers of this series.¹ Recently, however, we have made a number of changes and improvements in the apparatus that seem worthy of record as they have resulted in greatly increased accuracy and convenience, in the possibility of use of the method through wider ranges of concentration and materials, and in the use of the method under unfavorable circumstances.

2. Changes in the Design of the Cell

All of our recent work has been carried out with the type of cell designed by MacInnes and Brighton^{1c} in which the boundary is formed by means of a shearing motion. The improved apparatus is shown in Fig. 1. The disks B and C are now made of plate glass, instead of the hard rubber formerly used. The glass does not warp after a little use as the rubber did. It also has a smoother surface, and its transparency is frequently of service. The channels, etc., in the surfaces of the plates that are in contact were etched out with hydrofluoric acid.

Since the motion of a boundary through 10 cm. of the measuring tube involves a volume of only 1.7 cc., and in our most recently constructed cell only 0.32 cc., it is evident that all precautions must be taken to prevent slight volume changes in the apparatus that would, ever so slightly, affect the motion of the boundaries. In pressing the lubricated plates together a small amount of air was included under a slight excess of pressure. This was occasionally sufficient to form a bubble at the junction of the measuring tube and apparently produced irregularities in the readings. This difficulty was overcome by placing a vent, F in Fig. 1, which releases the pressure by leading off the excess of air from the space between the plates to a point above the level of the thermostat water.

It has been our practice to have one of the electrode vessels completely

¹ (a) MacInnes and Smith, *THIS JOURNAL*, **45**, 2246 (1923). (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924). (c) MacInnes and Brighton, *ibid.*, **47**, 994 (1925). (d) Smith and MacInnes, *ibid.*, **47**, 1009 (1925). (e) MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926).

filled with solution. The moving-boundary results are corrected, according to the method of Lewis,² for volume changes at this closed end of the apparatus. The other electrode vessel contains a bubble of air to allow for possible expansions and contractions during the electrolysis. Originally this bubble was at the top of the vessel which projected into the air and was thus exposed to changes of temperature. This was probably the cause of some irregularities in our measurements. At present, however, one of the tubes holding the electrodes is left hollow and holds a small volume of air under the solution where it encounters a uniform temperature.

An added convenience, which makes possible the turning Disk B over Disk D with a minimum of mixing due to shaking, is furnished by the chain and sprocket arrangement also shown in Fig. 1. The brass Disk A which extends beyond the water of the thermostat is connected to a small sprocket S by means of a brass tube which encircles the upright of the stand. The sprocket engages a chain which is passed around Disk B. The chain is held in place by means of a rubber band which is slipped over a strip of brass holding a pin which, in turn, is inserted into a hole bored in the glass disk. Thus by turning the brass Disk A, the glass Disk B can be swung into place.

The convenience in measuring the time required in the passage of a boundary between graduations of the measuring tube has been greatly increased by substituting a Veeder magnetic counter for the watch previously used. The counter is operated once per second, by an accurate pendulum clock. Electrical contacts with the pendulum have been avoided by making the pendulum interpose a screen between a light and photo-electric cell once per second. By amplification this is made to operate the electric counter. The latter is started when the boundary passes the first graduation mark, and readings are made directly in seconds thereafter. A large amount of burdensome computation (subtractions, and changing of hours and minutes into seconds) is thus avoided.

² Lewis, *THIS JOURNAL*, 32, 862 (1910).

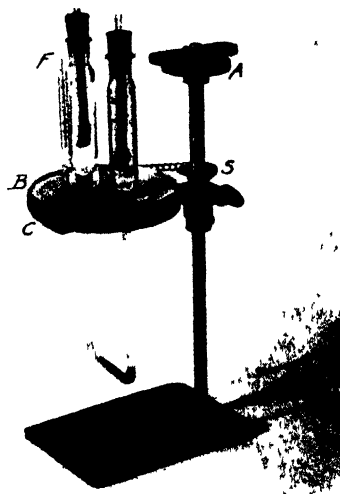


Fig. 1.

3. The Effect of Vibration

In our earlier experiments in Cambridge we found that erratic results were obtained if there were a large difference between the densities of the leading and indicator solutions, such as exists between silver or cesium nitrates and lithium nitrate. The boundary usually started at nearly the correct rate but gradually slowed down toward the end of the determination. This effect is undoubtedly due to mixing caused by waves, over the surface of the boundary, generated by external vibrations. By exercising ordinary care to remove sources of vibration, results were obtained even with silver solutions. However, after moving the apparatus to New York City the vibrations were found to be intense enough to make the moving-boundary method quite useless, even for pairs of solutions without large differences in density.

This serious difficulty was overcome, after a series of preliminary experiments, by the use of a modified Julius suspension for the thermostat. A diagram of the arrangement is shown in Fig. 2. The thermostat is placed on a cast-iron plate, *a*, from which four heavy bolts extend to about the level of the center of gravity of the suspended system. From these bolts extend four 4 cm. heavy coil springs, *c*, about 45 cm. long which, in turn, are supported by four light ropes, *d*, tied to hooks fixed in a heavy beam in the ceiling. Under these conditions no external vibrations of any strength reach the thermostat, as is shown by the steadiness of a beam of light reflected from the surface of a dish

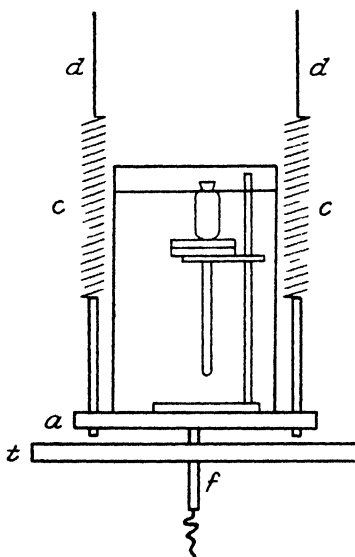


Fig. 2.

of mercury. Although these are ideal conditions for the progress of the measurements it is necessary to commence the determination, that is, to turn the electrode vessels into place over the measuring tube, without starting vibrations in the system. This we have accomplished as follows. The lower edge of the suspended system is hung very near to the table top *t*. From the center of the cast-iron plate, *a*, extends an iron rod, *f*, which passes through a hole in the table top and to which is attached a rope which is connected to a foot treadle (not shown in the figure). By pressing on this treadle the suspended system is temporarily placed in contact with the table. Choosing a moment when vibration is feeble, the boundary is made by turning Disk B (Fig. 1) on Disk C. The treadle is then carefully released. This can be done without causing the suspended system to swing.

It has been our frequent observation that a boundary which starts at an incorrect rate (due presumably to a very slight initial mixing of the solutions) will gradually approach the correct rate as the experiment proceeds, unless there is an additional source of disturbance. It appears, therefore, that the vibration during the time that the boundary is being formed and the suspended system is released cannot have an appreciable effect.

4. Experiments with Rising Boundaries

So far all our work has been carried out with indicator solutions which are lighter than the solution of which the transference number is to be measured. The indicator solution must therefore be on top of the leading solution and the boundary must descend during the determination. It seemed probable that a greater range of indicators would be available, including, possibly, some colored materials which might be visible at great dilutions, if a cell could be constructed which would utilize indicator solutions which are heavier than the measured solution. This would, of course, involve rising boundaries. Experiments were therefore carried out with an apparatus which was substantially the cell shown in Fig. 1 inverted, although a number of details had to be changed.

Observations were made on the boundaries KMnO_4 0.07 *N* \rightarrow KCl 0.1 *N*, and BaCl_2 0.07 *N* \rightarrow KCl 0.1 *N*. In both cases the boundaries were relatively sharp at the start, although somewhat convex upward. As they progressed, however, they became increasingly diffuse and instead of maintaining a steady motion as would be expected, the current being kept constant, both boundaries slowed down. It was evident that some additional condition governed the phenomenon when the boundaries were rising.

With the permanganate-chloride boundary there was another effect which was visible, due to the color of the indicator solution. A representation of the effect is shown in Fig. 3, in which the heavily shaded region, C, represents the portion of the tube containing the potassium permanganate indicator solution and the unshaded, B, the potassium chloride solution. Rising from the boundary was a faintly pink region of chimney shape, the color of which became more intense as the electrolysis proceeded, and finally not only this region but all of the potassium chloride region became colored. It immediately became of interest to find out whether a similar effect is to be observed with a descending boundary, and it was a relief to find that with permanganate as the leading solution and an acetate as indicator, a perfectly sharp boundary was formed with no pink color in the acetate solution. Furthermore, the boundary moved at the normal uniform rate.

The explanation of the disturbing effect with rising boundaries appears to be as follows. Since the indicator solution contains ions which have lower mobility than the ions of corresponding charge in the leading solu-

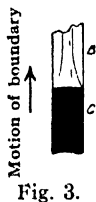


Fig. 3.

tion, and is further diluted according to the relation^{1a,3} $C/T = C'/T'$, the conductance of the indicator solution must be lower than that of the measured solution. The result is therefore that due to the higher potential gradient, more heat is generated in the indicator solution than in the solution it follows. The effect shown in Fig. 3 is due to the fact that a small amount of the potassium chloride solution immediately in contact with the boundary became warmed and rose, carrying a small amount of permanganate with it. A similar effect must have occurred in the barium chloride-potassium chloride boundary, but it was not visible. In the case of the descending boundary, on the other hand, the warmer indicator solution is on top, and the difference of temperature tends to keep the two solutions separate, if it has any effect at all.

It is evident, therefore, that in all moving-boundary measurements the solution of lower conductance must be on top. Some of the early work with the moving boundary must be in error on account of failure to observe this effect. An additional effect of heat generated in the apparatus will be given in Section 6.

5. The Visibility of the Boundary

In all our measurements we read, to the nearest second, the time when the boundary passes a given graduation mark. An increase of accuracy has been attained by graduating the tube as is shown in Fig. 4. The graduation marks extend on either side, one-fourth or less of the distance around the tube, leaving a clear space in front and back. In this way the boundary is always visible, and is never covered by the graduation mark. With faint boundaries, such as are obtained with dilute solutions, this arrangement is entirely necessary.

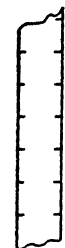


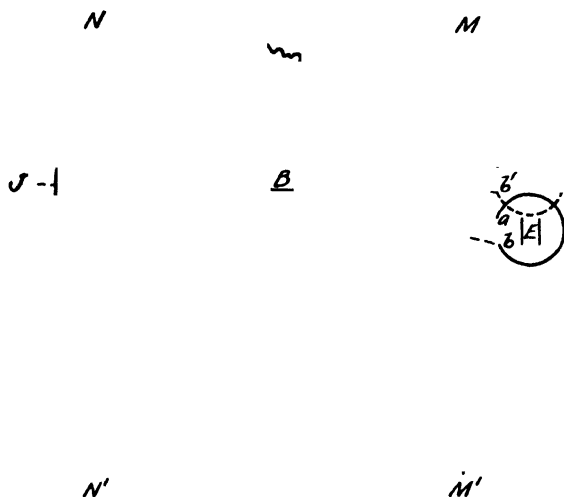
Fig. 4.

The possibility of distinguishing the junction of two transparent solutions depends upon the differences in their refractive indices. The arrangement now used for viewing the boundary is shown diagrammatically in Fig. 5. An electric lamp E is shaded by a metal screen except for a slit, $a-b$ (seen edgewise in the figure) which is covered by a translucent screen. By means of a rack, sprockets and chain this slit can be moved vertically. Ignoring the effects of the glass walls of the thermostat $M-M'$ and $N-N'$ and of the measuring tubes, the path of a beam of light from the lower edge b of the illuminated slit is b, B, J . Thus, the edge b , viewed *through the boundary*, appears as if it were at b' . At a certain limiting value of the angle $b B b'$ we have the condition for total reflection. At this point the boundary appears as a sharp dark line at b' with an illuminated area below it due to the fact that the illuminated slit can also be viewed directly through the lower solution. The apparent separation

³ C , C' , T and T' are, respectively, the concentrations and transference numbers of the measured and indicator solutions

of the direct and refracted images depends on the differences of the indices of refraction of the solutions meeting at the boundary.

A very surprising increase in the visibility of boundaries is obtained by the simple device of placing a lens at the point J as shown in the figure. The lens must have a focal length reaching only to the region of the boundary. The effect of this arrangement is to throw the directly viewed edge of the slit *b* out of focus. The edge of total reflection, which constitutes the boundary, can thus be much more readily distinguished. Other optical systems that we have tried have been less effective than the simple one just described.



6. Conditions Governing "Adjustment"

As explained in previous papers in this series, the ions of the leading solution and the indicator move at the same rate when the solutions are adjusted to the condition

$$C/T = C'/T' \quad (1)$$

which must be, in general, obtained by a series of experiments. A curve of the apparent transference numbers as ordinates against the indicator concentrations C' as abscissas takes an upward slope in the dilute region, then a horizontal portion followed by a slope for more concentrated indicators. The correct transference number, and the values fulfilling the condition of Equation 1 are on the flat portion of the curve.^{1d} Now the relative width of this flat portion is an important matter, since it determines the number of determinations that must be made in order to establish the shape of the curve. According to Kohlrausch⁴ and others

⁴ Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

the condition represented by Equation 1 should establish itself automatically, no limits of initial concentration being stated. However, we have found in general that this can only be relied on for deviations of 3 to 5% from the correct concentration. There are apparently additional influences, including diffusion, that limit the range of adjustment. We have found, for one thing, that adjustment is considerably modified by the amount of heat developed in the measuring tube. Some experiments already published^{1b} have shown that with an apparatus involving the use of a wide tube (10 mm.) the flat spot in the curve nearly disappeared. In that case, due to the relatively low ratio of external surface to area of tube, the heat had little opportunity to be conducted away. We have recently observed much the same effect with a 6mm. tube with more concentrated solutions, and thus necessarily higher currents than were used in the earlier experiments. On the other hand, we have found adjustment over wide ranges of indicator concentrations under two conditions, (a) very dilute solutions, and (b) solutions of electrolytes having high equivalent conductances. In the first of these cases it is evident that little heat is developed because small currents pass through the apparatus. The measurements with highly conducting solutions (for example, 0.1 *N* hydrochloric acid or 0.1 *N* nitric acid) can be explained in the same way. Since the resistance is relatively low, less heat is generated. However, this latter case is complicated by the fact that the solution is followed by an unusually dilute indicator solution (0.03 to 0.05 *N*) in which, due to the high potential gradient, the heating effect must be unusually large. However, this hotter solution is on top rather than on the bottom in contrast to the experiments described in Section 4, so that the small difference of temperature apparently increases the stability of the system rather than otherwise.

For use with solutions above 0.1 *N* we have constructed a cell with a thin-walled measuring tube with an internal diameter of only 2 mm. At the same rate of motion of the boundary this smaller tube requires only one-ninth of the current used in the 6mm. tube, whereas the surface exposed is one-third. A distinct increase of the range of indicator concentrations yielding adjustment has been observed, as would be expected. However, other factors not yet clearly understood affect adjustment. We expect to make this matter the subject of future investigations.

7. The Transference Number of 0.05 *N* Silver Nitrate Solution

The data we have accumulated on transference numbers will be published in an article dealing with the question of the ionization of strong electrolytes. It may be of interest, however, to give an example of the precision attainable, under favorable circumstances, by the moving-boundary method. A plot of the data on 0.05 *N* silver nitrate solution is

given in Fig. 6, in which the observed transference numbers are plotted as ordinates and the indicator concentrations as abscissas. The concentration of the indicator solution (lithium nitrate) varied from 0.0385 *N* to 0.0410 *N*. It will be seen that adjustment was attained through nearly all of this range within about 0.02%. A slight drop in the transference number can be observed in the region of the dilute indicator solutions. Experiments were not carried out at higher values of the indicator solution than those shown, but from analogy to other cases studied the curve would eventually ascend. The value for the transference number obtained, 0.4664 at 25°, is lower than published values by the Hittorf method, which are nearer 0.470.

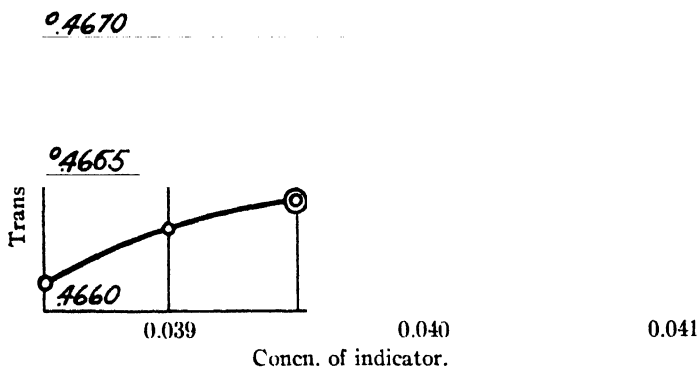


Fig. 6.

Summary

Improvements in the moving-boundary apparatus for determining transference numbers, leading to greater accuracy and convenience in the use of the method, are described.

The measurements have been found to be much influenced by vibrations, particularly where there is much difference in density of the solutions at the boundary. Our method for eliminating this difficulty is outlined.

Experiments are described with indicate that boundaries must be descending during the determinations. Ascending boundaries give rise to heat effects which cause mixing.

The conditions governing the visibility of boundaries are outlined.

Some of the factors governing "adjustment," that is, the dependence of the motion of the boundary on the indicator concentration, are outlined.

The precision of the method now attainable is shown by measurements of the transference number of 0.05 *N* silver nitrate solution.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

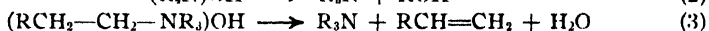
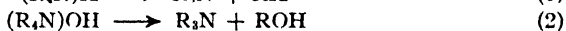
THE DECOMPOSITION OF QUATERNARY AMMONIUM HYDROXIDES. ALKOXYMETHYLDIETHYL-METHYL- AMMONIUM HYDROXIDES

BY T. D. STEWART AND JOHN G. ASTON

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The thermal decomposition of quaternary ammonium compounds usually proceeds according to one of three reactions.



The work of earlier investigators has been reviewed by v. Braun¹ who concluded that if the four R groups are not alike, the group which appears as RX (Equation 1) upon decomposition will depend upon the relative reactivities of the groups present. He arranged certain groups in the decreasing order of their reactivities as follows: allyl, benzyl, methyl, ethyl, propyl, *isobutyl*, *iso-amyl*, phenyl.

v. Braun also determined the order of reactivity of the various groups for the hydroxides (Equations 2 and 3) and found certain differences from the order given for other negative ions. In the order of decreasing reactivity he found them to be allyl, benzyl, ethyl, propyl, *iso-amyl*, methyl, *isobutyl*, phenyl. In another series of experiments he determined the effect of the length of the carbon chain and the effect of certain substitutions upon the tendency of the group to split off as compared to the methyl group, and concluded that the symmetry of the ethylene formed, together with certain factors regarding conjugation of the unsaturated groups, determined the velocity of the rupture.

Discussion of Results

The present paper deals with the decomposition of quaternary bases of the type $[ROCH_2-NR_3]OH$. Robinson and Robinson² distilled a solution of butoxymethyldiethyl-methylammonium hydroxide and found only methyldiethylamine among the basic decomposition products. This result has been confirmed in the case of the ethoxy derivative and would appear to indicate a higher degree of reactivity for the $(RO-CH_2-)$ group than for the ethyl group.

The fact that the tertiary bases hydrolyze readily in aqueous acid according to the equation $R'O-CH_2-NR_2 + H_2O + H^+ \longrightarrow R'OH + CH_2O + (R_2NH_2)^+$ suggests that this abnormal reactivity of the alkoxy-methyl group is to be associated with hydrolysis of the ether linkage. However, the quaternary salts decompose very slowly or not at all in

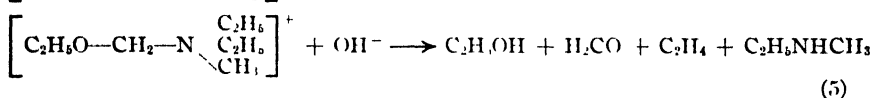
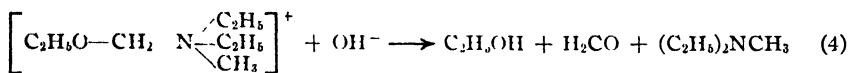
¹ v. Braun, *Ann.*, **382**, 1 (1911).

² Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

aqueous acid or dilute alkaline solutions at 100° and it will be shown that the same factors which cause the rupture from nitrogen of the alkoxy-methyl group also effect the rupture of the other alkyl groups. It will also be shown that the proportion of alkoxy-methyl to methyl or ethyl groups which split off is a function of the temperature.

The decomposition of ethoxymethyldiethyl-methylammonium hydroxide has been studied under three conditions. First, a solution of the base was evaporated slowly (during ten days) in a vacuum desiccator at room temperature; second, a similar solution was evaporated more rapidly (two days) at room temperature in a vacuum; third, a solution of the hydroxide was concentrated by distillation at atmospheric pressure.³

The results of the three experiments can be expressed by two equations.



The only difference between the first and second experiment was the time required for the decomposition. The products found were practically identical in the two cases, and indicated that 18.5% of the reaction took place according to Equation 4, and 81.5% according to Equation 5. The results of the third experiment, at the higher temperature, indicated that at least 90% of the reaction took place according to Equation 4.

The rate of rupture of the alkoxy-methyl and of the ethyl groups is thus the same function of the rate of pumping or rate of evaporation of water from the solution. As a solution of the base becomes concentrated at room temperature, no decomposition occurs until the sirupy liquid approaches a composition corresponding to between a tetra- and penta-hydrate. The reaction begins suddenly, proceeds at a constant rate, depending upon the surface exposed and the pressure, and stops as suddenly as it started.⁴

The relative activities of the three groups at room temperature are as follows: $\text{C}_2\text{H}_5 > \text{C}_2\text{H}_5\text{OCH}_2 > \text{CH}_3$. Above 100° the relative reactivities are $\text{C}_2\text{H}_5\text{OCH}_2 > \text{C}_2\text{H}_5 > \text{CH}_3$. It is apparent that the order of reactivity may be changed by a change in the temperature at which

³ This was the method used by nearly all of the previous investigators.

⁴ In one instance a sample contained in a weighing bottle was slowly evaporated for a week. It started to give off gas (ethylene and amines) within a given half-hour, and while held at constant pressure gave off gas bubbles only from the surface at practically constant rate, as measured by the time necessary to build up to a given pressure or as measured in other instances by a sulfuric acid bubbler in the line. The apparent equivalent weight remained constant throughout the decomposition.

the decomposition is carried out, and that the reactivity of the ethoxymethyl group is closer to that of ethyl than to that of methyl.

The decomposition of *isobutoxymethyl*-trimethylammonium hydroxide, $C_4H_9OCH_2-N(CH_3)_3OH$, under the same conditions as in the second experiment described above, yielded trimethylamine as the only volatile base.

The question of whether a tetrahydrate, a lower hydrate, or anhydrous molecule is the species which decomposes cannot be answered. If the evaporation and decomposition at room temperature proceed at a higher total pressure, and therefore more slowly, bubbles form throughout the mass instead of solely at the surface, suggesting that whatever is formed by evaporation at the surface has time to diffuse to some depth (about 1 to 2 cm.) before decomposing, or that water from the body of the solution has time to diffuse to the surface so that the composition is constant throughout the mass. In such a case the equivalent weight more nearly corresponds to that of a tetrahydrate than in the case of a more rapid evaporation where the surface layer only is kept at a composition which promotes decomposition. At a very low pressure (0.001 mm.) and temperature (-20°), evaporation proceeds slowly without apparent bubbling, but as soon as the temperature is raised, even at atmospheric pressure, evolution of gas begins. These facts seem to indicate that hydrate formation stabilizes the quaternary ion in the presence of hydroxide ion.⁵

Another important fact, namely, that hydroxide and carbonate ions cause the formation of ethylene as well as of alcohol, must be accounted for and possibly connected with the relative rates of rupture from the nitrogen of the various groups under consideration. It seems probable that the instability of an "onium" compound lies in the tendency of the charge on the central atom to become neutralized at the expense of a shared electron with the consequent loss of a positive ion.

The ease with which a quaternary ammonium compound will decompose will then depend upon two factors; first, the tendency of the nitrogen atom to lose the positive charge, with the loss of one of the groups as a positive ion, and second, the reluctance of the bound groups to split off as the positive ion. This reluctance is less if the presence of certain groups (ethylene bonds, oxygen atoms) may serve to distribute the positive charge along the group in question, and hence reduce the intensity of the positive charge upon the nitrogen atom. Another means of reducing the charge upon the nitrogen or upon the carbon atoms is the dissociation of a hydrogen atom. A reactive hydrogen upon an atom sufficiently

⁵ Very few quaternary bases decompose rapidly in dilute aqueous solution, even at 100° . Of these may be mentioned those of the type $[R_3NOR']OH$, which in dilute aqueous solution at room temperature slowly decompose to give the tertiary amine R_3N , water and the aldehyde or ketone corresponding to the radical R' . The substance $[C_6H_5CH_2CH_2-N(CH_2)_3]OH$ also decomposes in dilute solution, upon heating.

near the nitrogen, through its oscillation if not actual ionization, could in effect reduce the intensity of the charge upon the nitrogen and carbon, and facilitate the rupture reaction. The role of the hydroxide ion then becomes clear. It acts either as an agent to aid in the removal of hydrogen ion from the molecule, or to replace the tertiary amine nitrogen in the quaternary ion. The former reaction explains its specific action in hastening decompositions which do not take place in acidic solution and in causing the formation of ethylenes.⁶

The decomposition does not involve ions, in the sense that there exists at any time appreciable amounts of either alkyl or hydrogen ions in the solution, or that either of these ions is formed as a *reversible* first step in the decomposition. We may rather look upon the decomposition, when an ethylene is formed, as preceded by the *simultaneous* loosening of the carbon-nitrogen and carbon-hydrogen bonds. This is followed by the simultaneous loss of hydrogen ion, rupture of the carbon-nitrogen bond, and rearrangement of the carbon residue to a stable ethylene. The relative rates of the decompositions will then depend upon the capacities of the various groups to reduce the intensity of the positive charge through minor rearrangements of electrons and protons within the group. The loss of hydrogen ion to form water, in the presence of hydroxyl ion, will cause a more rapid rupture of a given group. If this last reaction could be excluded, it is probable that the relative rates of decomposition of different groups in salts and in quaternary bases would be identical.

The stabilizing effect of water upon the quaternary ion may be attributed to the same sort of factor that promotes the decomposition. The hydration of the ion serves to distribute the positive charge over what is essentially a larger molecule, thereby lowering the intensity of the charge upon the nitrogen. There is, therefore, less tendency for the carbons or hydrogens to assume a positive charge.

Experimental Part

Decomposition of Ethoxymethyldiethyl-methylammonium Hydroxide at Room Temperature

Expt. 1. Qualitative Decomposition.—A solution of ethoxymethyldiethyl-methylammonium hydroxide was prepared from 20.15 g. (0.074 equivalent) of the iodide and a slight excess of the calculated quantity of silver oxide. It was evaporated at room temperature in a vacuum desiccator over calcium chloride to a volume of about 25 cc., then transferred to a tared weighing bottle and the evaporation continued in a vacuum over phosphorus pentoxide. The solution became viscous and had no odor of amines. When the weight of the residue reached 15.80 g., a froth was observed on the surface, and amine and formaldehyde odors became noticeable. A sample taken at this point, when titrated with standard acid, using phenolphthalein as indicator, showed the

⁶ See Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 135.

equivalent weight to be 248, and the 15.80 g. to contain 0.0636 equivalent of base. The equivalent weight calculated for the tetrahydrate of the base is 235.

The decomposition was continued in a vacuum, the pressure rising at a constant rate from 2 mm. to about 25 mm. in two days. The cessation of the decomposition was abrupt at the end of ten days, leaving a liquid residue. The decomposition products were isolated as follows. Samples of gas aspirated from the desiccator were shown to be a mixture of ethylene and air by the usual methods of absorption and combustion. Most of the amines were contained in the acid drying agent and were recovered by the addition of alkali and by distillation into hydrochloric acid. The pure, dry hydrochloride weighed 5.14 g.

Anal. (Volhard). Calcd. for $C_5H_9NHCl \cdot Cl$, 37.15; for $C_5H_{13}NHCl$, 28.71. Found: 35.25.

The analysis corresponds to 18.5 mole % of methyldiethylamine hydrochloride and 81.5 mole % of methylethylamine hydrochloride, shown also as follows. A 4.34 g. sample of the mixed hydrochlorides (containing 0.00431 equivalent of chlorine) was separated by the method of Hinsberg⁷ into the tertiary amine and the benzene sulfonamide of the secondary amine. The yield of tertiary amine was 0.000915 equivalent, or 21% of the total amine in the mixed salts. The platinum double salt decomposed sharply at 230°.

Anal. Calcd. for $(C_5H_{13}NH)_2PtCl_6 \cdot Pt$, 33.37. Found: 33.33.

The yield of dry, liquid methylethyl benzenesulfonamide was 5.76 g.

Anal. (Kjeldahl). Calcd. for $C_9H_{13}NSO_2$: N, 7.04. Found: 6.96.

Upon hydrolysis, the amide yielded 2.08 g. of an amine hydrochloride; *m p*, 126–129.5°.

Anal. (Volhard) Calcd. for $C_5H_9NHCl \cdot Cl$, 37.15. Found: 36.90.

The chloroplatinate decomposed at 208–208.5°.

Anal. Calcd. for $(C_5H_9NH)_2PtCl_6 \cdot Pt$, 36.96. Found: 36.96.

The amines are thus methyldiethylamine and methylethylamine.⁸ The proportions of the two given by the chlorine analysis of the mixed salts are probably accurate to about 1%.

The residue from the decomposition was shown to contain salts of the undecomposed base by preparation and analysis of the chloroplatinate. When recrystallized from 50% alcohol the chloroplatinate decomposed at 223.5°.

Anal. Calcd. for $(C_5H_{10}ON)_2PtCl_6 \cdot Pt$, 27.87. Found: 28.00.

The salts were probably the bicarbonate and formate.

Expt. 2. Quantitative Decomposition.—A solution containing 0.0371 equivalent of ethoxymethyldiethyl-methylammonium hydroxide was prepared and concentrated as above. Its equivalent weight was 267 when the decomposition began. As soon as decomposition became evident, the weighing bottle and contents were sealed into a 100cc. tube (Fig. 1), which was sealed to a system consisting of a liquid-air trap (3 cm. \times 35 cm.) connected, through a tube containing phosphorus pentoxide, to a hand-operated Töpler pump. The line was pumped out by means of the Töpler pump to 2 mm., at which pressure the liquid in the weighing bottle started to boil. This boiling soon ceased. The system was evacuated to 0.5 mm. At this pressure vigorous decomposition took place and continued for 52 hours.

⁷ Hinsberg, *Ber.*, **38**, 906 (1905).

⁸ The chloroplatinates decompose, respectively, at 231° (Ref. 2) and 207–208° [Beilstein, vol. 1, p. 1125]. Hinsberg [*Ann.*, **265**, 180 (1891)] describes methylethylbenzene sulfonamide as a liquid.

After 52 hours, the decomposition stopped as suddenly as it had started, very little material remaining. The liquid air around the trap was replaced by a mixture of solid carbon dioxide and ether. This allowed the ethylene to boil out of the trap and the pressure in the line rose to about $\frac{2}{3}$ atm. The system stood overnight in this condition in order to allow time for the formaldehyde to polymerize. The outlet from the pump was then connected to an aspirator (Fig. 2) filled completely with mercury. The ethylene was pumped out of the line into the aspirator until the residual pressure was

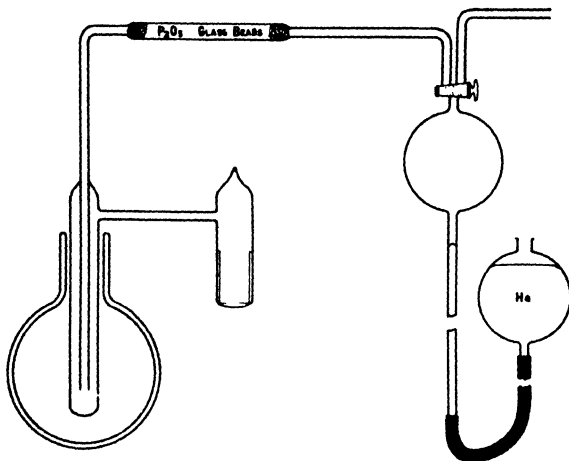


Fig. 1.

11 mm., the displaced mercury being collected in a weighed receiver.⁹ The pressure in the aspirator was finally adjusted to atmospheric pressure by leveling the mercury surfaces in the bulb and reservoir of the pump at the three-way stopcock. During the process the adjustable tip forming the outlet of the aspirator was kept below the mercury surface in the receiver, the latter being kept below the mercury level in the bottle. The mercury in the receiver was then weighed.

The 8091 g. of mercury (596 cc.) displaced by ethylene at 19.1° and 757.1 mm. pressure corresponds to 0.0247 mole of ethylene.

Analysis of the gas showed the absence of amines and the presence of only traces of formaldehyde. A sample was completely absorbed in bromine water. The ethylene remaining in the system was estimated from the volume and residual pressure and the probable amount dissolved in the liquid mixture of amine, alcohol, formaldehyde, etc., at -77° , to be about 0.0012 mole. The total ethylene formed was thus 0.0259 mole and corresponded to the amount of methylethylamine formed (0.0263 mole) within experimental error.

After removal of the ethylene, dry air was let into the line and an excess of acid added to the trap, while still in the carbon dioxide-ether mixture. The solution of

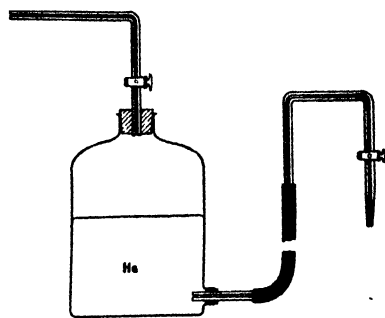


Fig. 2.

⁹ Pumping was not continued further for fear of pumping over formaldehyde. A correction for the remaining ethylene is made later.

amine hydrochlorides was transferred to a large flask and steam-distilled from acid solution to separate the formaldehyde and amines. The solution was then made alkaline and the amines were distilled into a known volume of standard hydrochloric acid which was then back-titrated. The phosphorus pentoxide from the tube was dissolved in water and treated in a similar manner. There was found in the trap 0.03235 equivalent of volatile base and a negligible quantity in the phosphorus pentoxide.

The amines were distilled from an alkaline solution of the titration mixture into an excess of hydrochloric acid, and the water was evaporated, yielding 3.238 g. of mixed hydrochlorides.

Anal. (Volhard). Found: Cl, 35.25.

This analysis corresponds to 18.5 mole % of diethylmethylamine, and 81.5 mole % of methylethylamine. A weight of salt corresponding to 0.01207 mole of the hydrochloride was treated with benzene sulfonyl chloride to separate the secondary and tertiary amines as described above. Tertiary amine corresponding to 0.00181 mole was obtained. Assuming this to be diethylmethylamine, as in the previous experiment, this corresponds to 15.0 mole % of the decomposition. The value calculated from the chlorine analysis is to be taken as the more accurate, the estimated accuracy being about 1%.

Identification of Residue.—The residue in the weighing bottle weighed 0.8996 g. This was dissolved in water, yielding a solution neutral to phenolphthalein. On boiling, it became alkaline to phenolphthalein. Small quantities of 0.1 *N* sulfuric acid were added and the solution boiled after each addition, until the pink color appeared. Finally, the pink color no longer returned, showing all of the carbon dioxide to have been expelled. The excess of acid was then back-titrated; 0.00101 equivalent of 0.1 *N* sulfuric acid was used.

An excess of sulfuric acid was added and the mixture was steam-distilled, keeping the volume very low, until no more acid came over. The distillate was titrated with 0.1 *N* sodium hydroxide; 31.38 cc. was required. The formic acid was identified by reduction of mercuric chloride; found, 0.00101 equivalent of bicarbonate and 0.00314 of formate; total, 0.0042 equiv. of acid. The nitrogen in the residue from which the formic acid had been distilled was determined by the Kjeldahl method; found, 0.0044 equivalent of nitrogen, which agrees with the quantity of acid found within experimental error.

Expt. 3. High-Temperature Decomposition of Ethoxymethyldiethyl-methylammonium Hydroxide.—0.0455 equivalent of ethoxymethyldiethyl-methylammonium hydroxide in a solution of about one equivalent per 1000 g. was taken for the decomposition. The material was contained in a 500cc. Kjeldahl flask with glass beads to prevent foaming. The Kjeldahl flask was fitted with a spray trap and condenser, the latter dipping below an excess of 0.1 *N* hydrochloric acid. The flask was heated to 135° by means of a glycerol bath. At this temperature boiling took place. Almost as soon as distillation commenced, decomposition set in, as indicated by a piece of moist red litmus in the condenser turning to blue, and by the odor of formaldehyde in the receiver. The main part of the decomposition was carried out at 140–150°. When three-fourths of the liquid in the flask had disappeared, the decomposition became much more rapid. These observations seem to indicate only a slight decomposition through hydrolysis in the first stage and that the main decomposition took place after the liquid reached a low water content, just as in the low-temperature decomposition.

After the apparatus had reached temperature equilibrium, only two or three bubbles of gas escaped, showing that no permanent gas was formed.

When all of the material had decomposed, water was run into the flask and the amines were swept out by steam. Back-titration of the distillate showed the formation

of 0.03659 equivalent of volatile base.¹⁰ The distillate, after being acidified and steam-distilled, was made alkaline, and the volatile amines were collected in an excess of hydrochloric acid. The solution, after evaporation, yielded 4.61 g. of hydrochloride. Before analysis, the hydrochloride was evaporated with absolute alcohol to remove hydrochloric acid.

Anal. (Volhard). Calcd. for $C_6H_{13}NHCl$: Cl, 28.7. Found: 29.4.

This shows that decomposition took place to yield at least 90% of methyldiethylamine.

Expt. 4. Dehydration of Ethoxymethyldiethyl-methylammonium Hydroxide at -15° .—A quantity of ethoxymethyldiethyl-methylammonium hydroxide solution, prepared as above (equivalent weight, 267, at the decomposition concentration), was placed in a container cooled to -15° and a vacuum below 10^{-3} mm. maintained. After three days, no crystals having appeared, the flask was allowed to come to room temperature, when decomposition took place for a considerable time without pumping. A crystalline hydrate could not be obtained.

Preparation of *iso*Butoxymethyl-trimethylammonium Iodide and Hydroxide.—Dimethylaminomethylisobutyl ether was prepared as described by Robinson and Robinson;² b. p., $127-128.5^\circ$; equivalent wt., 132 (calcd., 131). This compound in 50% ether solution reacts explosively with methyl iodide, at room temperature. A 20% solution of the base in anhydrous ether was cooled in ice, and a 10% excess of methyl iodide in 40% anhydrous ether solution was added, taking care to keep out moist air. A white precipitate formed. When all of the methyl iodide had been added, the solution was removed from the ice and allowed to stand at room temperature for three days. The gelatinous mixture was diluted with dry ether and filtered. The salt was washed with ether and dried; m. p., $110-114^\circ$. (In one sample, melting started at 99° and then, almost immediately, the small amount of liquid resolidified. After further drying of the sample, the same phenomenon was noted.) The substance was crystallized from hot butyl alcohol (1 cc. per g.). The recrystallized product (m. p., $103-110^\circ$), after several crystallizations, had the same melting point. Other alcohols, tried as solvents, gave no better results. The compound is very soluble in water and alcohols.

Anal. (Volhard). (Uncrystallized material.) Subs., 0.3290, 0.2774: 12.56, 10.56 cc. of 0.0958 *N* $AgNO_3$. Calcd. for $C_8H_{20}ONI$: I, 46.50. Found: 46.4, 46.3. (Crystallized material.) Subs., 0.4600, 0.5106: 17.68, 19.66 cc. of 0.0958 *N* $AgNO_3$. Calcd. for $C_8H_{20}ONI$: I, 46.50. Found: 46.7, 46.7.

0.0448 mole of *isobutoxymethyl*-trimethylammonium iodide in 100 cc. of water was shaken with a slight excess of silver oxide until the solution no longer gave a test for iodide ion. The silver iodide was filtered off and the solution evaporated as described for the other quaternary bases. Only a very faint odor of amines was perceived.

About 0.004 equivalent of the base was neutralized with hydrochloric acid and the solution evaporated at room temperature over phosphorus pentoxide in a vacuum. The residue was taken up in absolute alcohol and the calculated quantity of chloroplatinic acid in alcohol was added. The platinum double salt was filtered off and washed with alcohol and ether; decomp. at $229.5-230^\circ$ (heating started at 20°).

Anal. (Ignition). Subs., 0.2776: Pt, 0.0780. Calcd. for $C_{12}H_{40}O_2N_2PtCl_6$: Pt, 27.87. Found: 28.13.

After recrystallizing, a constant decomposition point $231-233^\circ$ was obtained under

¹⁰ Complete decomposition was probably prevented, as in the room-temperature decomposition, by the formation of formic acid from the formaldehyde, according to the equation $2H_2CO \rightarrow HCO_2H + CH_3OH$.

the same conditions. Since the iodide is hard to purify, the decomposition point of the platinum salt may be used to characterize the base.

Anal. (Ignition). Subs., 0.1754: Pt, 0.0490. Calcd.: Pt, 27.87. Found: 27.93.

Expt. 5. Decomposition of *iso*Butoxymethyl-trimethylammonium Hydroxide at Room Temperature.—The remainder of the solution of the base, after evaporation over phosphorus pentoxide until decomposition took place, weighed 7.51 g. and had an equivalent weight of 231; 0.0325 equivalent of base was thus present. (Calcd. for the tetrahydrate, equiv. wt., 235.) The material in a weighing bottle was sealed up in the line already described (Fig. 1), the trap being surrounded by liquid air, and the line evacuated to 1.5 mm. Further evacuation was not possible because, if the decomposition became too vigorous, serious frothing took place. The decomposition continued for seven weeks.

When the decomposition was complete, the liquid air was replaced by a solid carbon dioxide and ether mixture. There was no increase in pressure in the line, showing that no ethylene was formed.

Air was let into the line and the amines were isolated as the pure hydrochlorides, as before; 0.0028 equivalent of base was found in the phosphorus pentoxide and 0.0204 in the trap; total, 0.0232 equivalent. (The rest of the base could be accounted for in the residue.)

Anal. (Volhard). Calcd. for C_3H_9NHCl : Cl, 37.15. Found: 37.10, 37.11.

A platinum double salt prepared from this hydrochloride was recrystallized from hot 67% alcohol. Its decomposition point, starting with the bath at 236°, was 240–241°.¹¹

Anal. (Ignition). Subs., 0.2152: Pt, 0.0794. Calcd. for $(C_3H_9NH)_2PtCl_6$: Pt, 36.96. Found: 36.90.

The decomposition thus yields trimethylamine as the only amine.

Expt. 6. Decomposition of Dimethyldiethylammonium Hydroxide at Room Temperature. Decomposition of Normal Carbonate.—Diethyldimethylammonium hydroxide was decomposed by evaporation of a solution in a vacuum desiccator at room temperature. Ethylene, dimethylethylamine and water were the only products formed.

An attempt was made to obtain a crystalline normal carbonate by the evaporation of an aqueous solution of diethyldimethylammonium carbonate at room temperature. Decomposition took place in the concentrated solution, and when an anhydrous solid eventually formed it proved to be the corresponding bicarbonate. This in turn, upon heating, did not give the normal carbonate, but only ethylene, pure ethyldimethylamine, carbon dioxide and water.¹²

Expt. 7. The Conductivity of Fused Ethoxymethyldiethyl-methylammonium Iodide.—Anticipating a high specific conductivity of the fused material, the cell shown in Fig. 3 was designed and used for the measurements. The distance between the electrodes was approximately 20 cm. and the cross-sectional area 0.1 sq. cm. The bulbs facilitated the filling of the cell, each being fitted with a calcium chloride tube to protect the material from moisture.

¹¹ Knorr [*Ber.*, 22, 184 (1889)] gives the decomposition point of trimethylamine chloroplatinate as 240–245°.

¹² The authors are indebted to Mr. R. D. Fowler for this result.

The conductivities were measured by comparison with corresponding resistances of a 9999ohm resistance box, using a Leeds and Northrup bridge for the comparison. The cell constant was determined by filling the cell with 1 *N* potassium chloride solution and determining the conductivity at 25°.

About 10 g. of recrystallized ethoxymethyldiethyl-methylammonium iodide (m. p., 84°) was placed in one of the bulbs and the cell immersed in an oil thermostat at 110°. When the material had melted it was drawn from one bulb to the other until the portion of the cell between the electrodes was entirely full.

After the material had been in the thermostat for half an hour, the conductivity was measured, and then again after one hour. No change was observed. The minima were poor and could not be improved by capacity adjustments. A lower conductivity than was expected prevented readings being taken in the middle of the bridge. These two factors introduce an uncertainty of about 5% in the measurements.

The conductivity was determined periodically over an interval of 12 hours, and found to remain almost constant. The temperature of the thermostat was then raised by steps to 140°, the conductivity being determined at intermediate temperatures and at 140°, in order to determine the effect of viscosity. On cooling to 110°, the conductivity had only changed slightly from its original value. A test showed that the material had almost completely decomposed.

An experiment showed, however, that no appreciable decomposition took place on keeping the original material at 110° for one hour. Further,

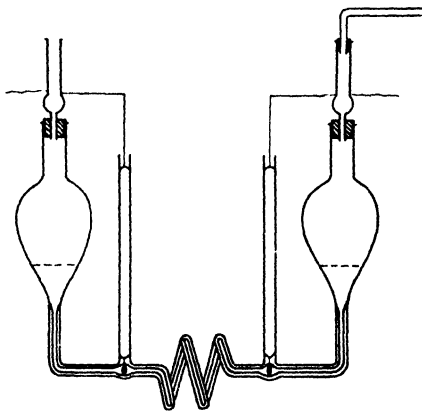


Fig. 3.

TABLE I
CONDUCTIVITY OF THE FUSED SALT^a

No.	Time in thermostat hrs	Temp., °C.	Resistance of cell, ohms
1	0.5	110	19,100
2	1	110	20,400
3	3	110	18,400
4	6	110	18,600
5	18	127	11,000
6	24	135	9,000
7	30	139	7,660
8	60	110	15,300

^a Cell constant = 245.

the fact that the conductivity of the material changed but slightly on standing at 110° shows that the impurities had little effect on the conductivity. The conductivity at 110°, after half an hour, may thus be assumed not in error by more than 10%. The results are given in Table I. From No. 1 we calculate $\kappa_{110^\circ} = 0.0128$ mho. The density of the fused salt at 110° was found to be 1.3615 g./cc. From these data we calculate $\Lambda_{110^\circ} = 2.56$.

Summary

*iso*Butoxymethyl-trimethylammonium iodide and hydroxide have been prepared. The electrical conductivity of fused ethoxymethyldiethyl-methylammonium iodide has been measured at 110°.

The decompositions of ethoxymethyldiethyl-methylammonium hydroxide and *isobutoxymethyl*-trimethylammonium hydroxide, on dehydration of the solution at room temperature, have been studied and compared with those of simple quaternary ammonium hydroxides under the same conditions. Ethoxymethyldiethyl-methylammonium hydroxide yields 18.5 mole % of diethylmethylanine and 81.5 mole % of ethylmethylanine, with a corresponding amount of ethylene; *isobutoxymethyl*-trimethylammonium hydroxide yields only trimethylamine. Above 100° the former base yields only diethylmethylanine, upon decomposition. A mechanism similar to that in the decomposition of the simple quaternary ammonium hydroxides is involved. The theory of such decompositions is discussed.

Attempts to prepare crystalline hydrates and anhydrous forms of the above hydroxides failed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

EXTRACTION OF MALTASE FROM YEAST¹

BY V. K. KRIEBLE, E. L. SKAU AND E. W. LOVERING

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Some years ago we were anxious to prepare an active maltase solution to repeat the experiments of Hill² on the action of maltase on a strong glucose solution. As we never succeeded in obtaining a very active maltase solution by the methods given by Hill, we decided to learn more about the extraction of maltase.

We were handicapped by not being able to obtain fresh bottom yeast which is richer in maltase than top yeast. We are, however, very much indebted to the Fleischmann Yeast Company for supplying us at all

¹ Read before the Organic Section of the American Chemical Society in April, 1924, at Washington, D. C.

² Hill, *J. Chem. Soc.*, 73, 634 (1898).

times with their baking yeast, a top yeast—in fact, without their assistance this research would have been impossible.

We soon learned that the heating and fine grinding recommended by Hill did not assist in the extraction of the enzyme. Further experiments showed that previous investigators had not recognized the marked effect of temperature, hydrogen-ion concentration and time on the rates of extraction. Neither had the difference between the rates of extraction from fresh yeast and dried yeast been recognized. When full allowance is made for these factors, many of the contradictory statements in the literature in regard to the content and extraction of maltase from fresh and dry yeast become intelligible.

Experimental Part

Preparation of the Yeast.—The pressed yeast consisting of pure yeast cells and containing about 70% of water was either extracted directly or else dried by the following method. The yeast was forced through a 40- or 60-mesh sieve with a pestle and the resulting threads of yeast were spread on glass plates in front of an electric fan operated at a moderate speed for 18 to 24 hours. The yeast at this stage is crisp and brittle and varies in color from light yellow to brown. It was then ground to a powder and put in a vacuum desiccator over phosphorus pentoxide until constant in weight. Yeast dried in this fashion retained its original maltase activity even after nine months.

Extraction of the Yeast.—Three extraction media were used, namely, 4.6 g. of disodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, 2 g. of magnesium carbonate and 4.6 g. of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + 6$ cc. of *N* sodium hydroxide solution for 80 cc. of solution in each case. These media gave a *PH*, after the yeast was added, of 8.3 to 8.5, 10 to 10.5 and 11.5 to 12, respectively. In each case, the yeast was ground in a mortar with some water and the substance to be used for extraction. It was then rinsed into a flask and diluted to make 80 cc.; 1 cc. of toluene was added and the flask put into a thermostat. At intervals the flask was thoroughly shaken and a sample removed.³

³ Some experiments were carried out to determine the effect of shaking the yeast in the extraction medium in a shaking machine operated at a slow rate. We used dry yeast and a solution of disodium phosphate for extraction. A parallel set of experiments was carried out where the flasks containing the yeast and phosphate solution were hung in the same thermostats with the following results.

Time of extraction, hrs.	$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{1}{4}$	3	4	26
Standing	0.42	0.56	0.67	0.67	0.84	0.71
Shaking	.43	.56	.65	.72	.78	.62

Shaking, therefore, does not appear to help very much and, in fact, is somewhat harmful if continued for a number of hours. The values given above, as well as in all other tables, represent decrease in rotation in degrees on a 2% maltase solution determined as described later.

The rapid and complete removal of the cells from the extract proved somewhat difficult. We tried at first to filter through a Büchner funnel and then through a Mandler filter. This is essentially Hill's method and removes the cells but requires large amounts of extract and a good many filter candles. It was found that filtering through a filter plate covered with a dense damp paper worked equally well. Occasionally, the filtrate had to be filtered a second time. By this method both the time of filtration and the amount of media necessary were cut down. The following table gives a comparison of the two methods.

	A	B	C	D
Plate filtration	0 42	0 56	0 71	1 31
Mandler filtration	.42	58	.69	1.25

Plate filtration was used in nearly all of the experiments reported. The only difficulty encountered was in the final stages of autolysis when the filter clogged badly, thus delaying the filtration.

Later on, we had the use of a large centrifuge and carried out a few experiments using the same yeast, extraction medium, temperature and time of extraction, but freed half of the extract from cells by the centrifuge and the rest by the method already described, with the following results.

Time of extraction, hrs	14	17 5	19 5	26
Centrifuge	0 92	0 96	0 94	0 62
Usual filtration	.91	93	.86	63

The centrifuge does not remove all the yeast cells, but apparently the few that are left have small influence so far as the apparent maltase hydrolysis is concerned.

The Activity of the Extract.— A definite amount of the filtrate, which was always slightly alkaline, was neutralized to litmus with a 1% solution of potassium dihydrogen phosphate. One cc. of this neutralized extract was added to 20 cc. of either a 2 or 5% solution of maltase hydrate, buffered with phosphates to a P_H of -6.5 to -6.7 , previously warmed to 30° . The hydrolysis was allowed to continue for 40 minutes at that temperature. Ten drops of glacial acetic acid were then added to stop the action, and one cc. of aluminum cream to aid in filtration. The volume was made up to 25 cc. and the solution immediately filtered. The extent of the hydrolysis was determined polarimetrically, using a 2-dcm. tube. Blanks were run in all cases.

As just stated, 1 cc. of the neutralized extract was used for hydrolysis but all the results in the following curves have been corrected for 1 cc. of the unneutralized extract which corresponds to the maltase taken from 0.1 g. of dry yeast. In making this correction, which was small, it was assumed that the amount of hydrolysis was directly proportional to the

amount of enzyme present—a rule found to hold for small changes in enzyme concentration when the amount of substrate is large.⁴ The ordinates on all of the following curves represent the decrease in rotation of a maltase solution caused by the enzyme extracted from 0.1 g. of yeast when it was allowed to act on the sugar solution for 40 minutes at 30°.

Effect of Temperature on the Extraction of Maltase from Dry Yeast.—

Fig. 1 represents what happens when dry yeast is extracted with sodium phosphate at various temperatures. It is obvious that the rate of extracting the enzyme from the cell increases with temperature. The amount of active enzyme in the extraction medium reaches a maximum, different at each temperature, and then falls off. Apparently, the best conditions for its extraction are not the best for its preservation. So long as the rate of extraction of maltase exceeds the rate of inactivation,

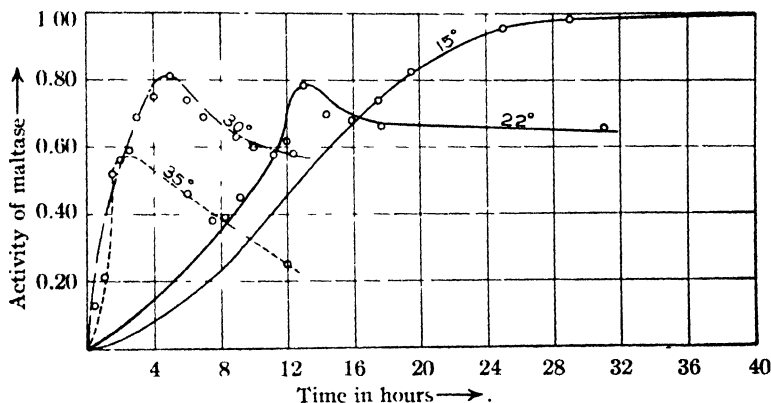


Fig. 1.— Na_2HPO_4 extraction of dry yeast at various temperatures.

the activity increases but when the rates are reversed, the activity falls. It is much easier to obtain a strong maltase solution at a lower temperature as the destruction is slower; furthermore, it is easier to stop extraction at the maximum activity. Similar results were obtained with the other two extraction media.

The Effect of the Hydrogen-Ion Concentration on the Extraction of Maltase from Dry Yeast.—Hill² first pointed out that associated with the autolysis of the yeast cell and the extraction of the maltase, there is a production of acidity in the extraction medium. This has also been observed by Emmerling, Willstätter and others. Most of these investigators neutralized this acid with a solution of sodium hydroxide or ammonium hydroxide or else added a buffer to take care of it. No one, however, has made a systematic study of the effect of the reaction of the medium on the extraction. Fig. 2 gives the activity of maltase obtained

⁴ Bayliss, "The Nature of Enzyme Action," Longmans, Green and Co., London, 1919, 4th ed., p. 107.

at 30° by three different extraction media, having a hydrogen-ion concentration varying from 8.3 to 12. Similar results were obtained at other temperatures. It is obvious that one needs a buffer near neutrality for obtaining the most active extract.

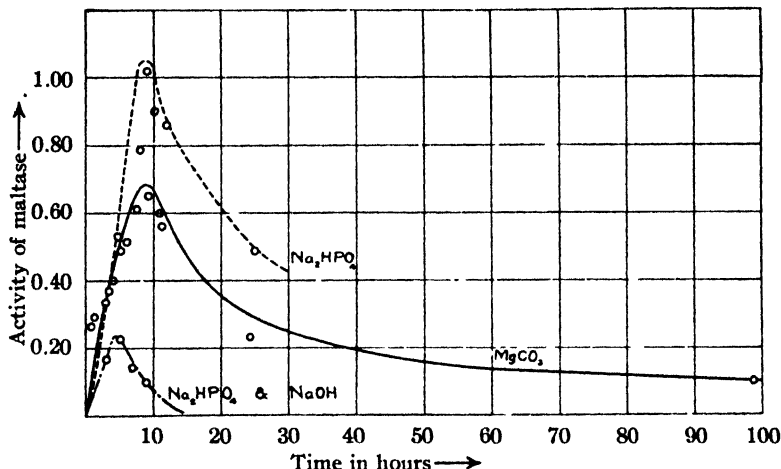


Fig. 2.—30° extraction of dry yeast at various P_H values

The Effect of Hydrogen Ion, Temperature and Time on the Extraction of Maltase from Fresh Yeast.—Figs. 3, 4 and 5 show what happens when the extraction medium and temperature are varied, using fresh yeast. These experiments were all carried out on the same sample

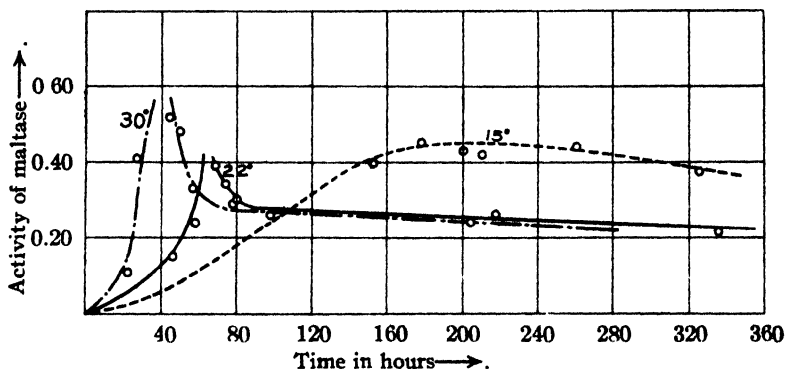


Fig 3.— Na_2HPO_4 extraction of fresh yeast at various temperatures.

of yeast. The extraction in all cases is very much slower with fresh yeast than with dry yeast, as the time scale is different in Figs. 3, 4 and 5 from that used in Figs. 1 and 2. It is apparent that the hydrogen-ion concentration in the extraction medium is not nearly so important with fresh yeast as it is with dry yeast, as the maximum activity observed for a

given temperature is almost the same for the three hydrogen-ion concentrations studied. With dry yeast there was in some cases a four-fold difference. The effect of the temperature at which the extractions are made is also different between the fresh and the dry yeast; 15° seems to be the best for the dry yeast, whereas 30 or 35° is somewhat more

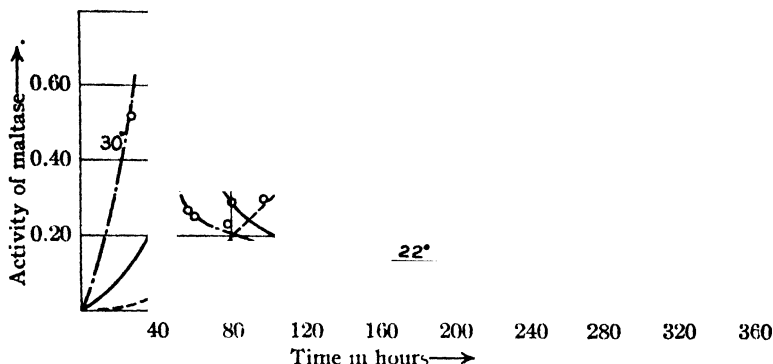


Fig. 4.— MgCO_3 extraction of fresh yeast at various temperatures.

favorable for fresh yeast. Fig. 6 also illustrates this point. This diagram also brings up another very interesting fact, namely, the great difference in samples of yeast. The greatest activity observed in Fig. 6 is nearly 100% higher than that observed in Fig. 3, a corresponding experiment on another sample. We found even greater differences at times between

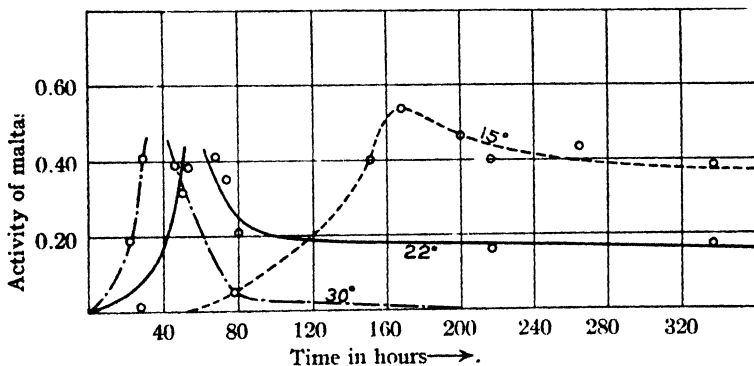


Fig. 5.— $\text{Na}_2\text{HPO}_4 + \text{NaOH}$ extraction of fresh yeast at various temperatures.

samples which appeared to be perfectly fresh. Whether this is due to the age of the cells, the time interval during shipment, or to the media in which it was grown we are unable to say. It is not due to experimental error, for the results could be checked with the same sample of yeast within a few hundredths of a degree on the polariscope.

Willstätter,⁵ describes a method to determine the amount of maltase

⁵ Willstätter, *Z. physiol Chem*, 111, 157 (1920).

in yeast quantitatively. We followed the method as given and found that the extract which corresponds with 0.256 g. of dry yeast caused a decrease of 0.64° in a 5% buffered solution of maltose hydrate. A part of this same sample of yeast was dried and extracted with disodium phosphate as already described. At the maximum of the extraction curve, 0.1 g. of dry yeast caused a decrease of 0.84° in a 5% buffered solution of maltase hydrate. As the maximum point on our curve can hardly represent the total amount of maltase present, it would appear that Willstätter's method cannot be considered as a quantitative method.

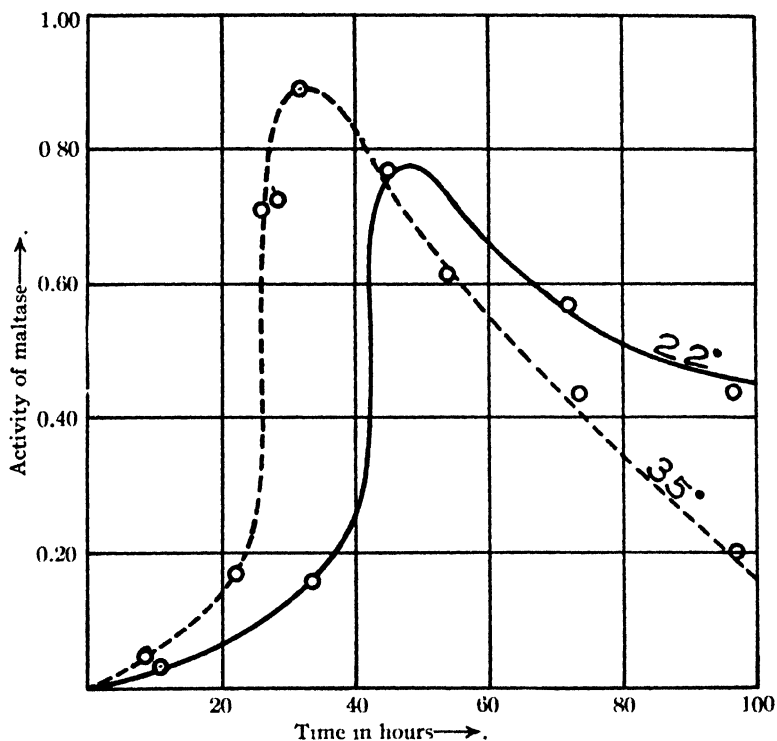


Fig 6.-- Na_2HPO_4 extraction of fresh yeast.

Summary

1. The rate of extraction of maltase from dry yeast varies with temperature. The lower the temperature, the slower the rate.
2. The maximum activity of the maltase extract obtainable from dry yeast varies with hydrogen-ion content of the extraction medium. The more nearly neutral the extraction medium, the more active the extract obtainable.
3. The rate of extraction of maltase from fresh yeast is always slower than from dry yeast.

4. The amount of alkali added to the extraction medium is not as important with fresh yeast as with dry yeast.

5. With dry yeast, 15° is a more satisfactory temperature for extraction than 30°, while with fresh yeast the reverse is true.

HARTFORD, CONNECTICUT

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE PREPARATION OF β -TRIPHENYLETHYLAMINE. REARRANGEMENT OF β -TRIPHENYLPROPIONHYDROXAMIC ACID

BY LESLIE HELLERMAN

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The preparation of β -triphenylethylamine, $(C_6H_5)_3CCH_2NH_2$, was required in one of a series of researches now in progress in this Laboratory on the mechanism of the oxidation of compounds containing the primary amino group. In order to approach the problem of the exact nature of intermediate products formed when a primary amine of the type RCH_2NH_2 , for example, is oxidized (for instance, in alkaline solution by halogen or by alkyl hypohalite) it was considered desirable to start with a substance of such structural properties that the intermediate products of its oxidation might reasonably be anticipated to possess considerable stability. A consideration of the structure of β -triphenylethylamine, where R is the triphenylmethyl group, from this point of view led to the selection of this substance as a decidedly promising starting product for investigation. It is to be noted, moreover, that this amine possesses potentially reactive hydrogen atoms only on the carbon atom adjacent to the amino group.

The synthesis of β -triphenylethylamine was first attempted by Elbs,¹ who reported that the amine resulted when triphenyl acetonitrile, $(C_6H_5)_3CC\equiv N$, was reduced in alcoholic solution with zinc and hydrochloric acid. Elbs gave a description of the compound, assigning a melting point of 116°, and also reported the preparation of the hydrochloride and the chloroplatinate. No melting point was given for the latter substance and no analyses whatsoever were reported. Later Biltz² reported that he was unable to reproduce the work of Elbs. An exhaustive study of the action of zinc upon the nitrile under varying conditions of solution, concentration and acidity failed to produce a method for the preparation of the amine. Biltz found, indeed, that the nitrile was reduced only³

¹ Elbs, *Ber.*, **17**, 700 (1884)

² Biltz, *Ann.*, **296**, 253 (1897)

³ Compare the stability of triphenyl acetonitrile toward hydrolysis, E. and O. Fischer, *Ann.*, **194**, 262 (1878).

by sodium in the presence of alcohol. But here triphenylmethane and hydrocyanic acid were the only products of reduction found in the reaction mixture. No amine was present.

The writer has verified the results reported by Biltz in every particular. Attempts to obtain the desired amine by reduction of triphenyl acetonitrile have resulted in complete failure. Sodium and alcohol have, as reported by Biltz, been found to effect reduction of the nitrile quantitatively to triphenylmethane and hydrocyanic acid.⁴

In view of the failure of reduction methods⁵ to produce β -triphenylethylamine it was considered best to attempt the preparation of the amine by rearrangement of the corresponding halogenamide, $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}(\text{Hal})$, or hydroxamic acid derivative, $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHOH}$. For this purpose it was necessary to prepare β -triphenylpropionic acid, $(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{COOH}$, in suitable yield. Henderson's⁶ method, which uses the action of triphenylbromomethane upon diethyl malonate with subsequent hydrolysis and loss of carbon dioxide leads to a pure acid but in unsatisfactory yield. A modification, tried in this work involving the use of cyano-acetic ester in place of malonic ester, did not lead to improved yields. By far the best way to prepare the acid is by the reaction of triphenylcarbinol and malonic acid.⁷ It has been found that the yield of β -triphenylpropionic acid is not quantitative as reported, but is very good in comparison with yields given by other methods. The amide of this acid, $(\text{C}_6\text{H}_5)_3\text{CCCH}_2\text{CONH}_2$, may be prepared by the usual methods. From the amide a derivative possessing the composition of a dichloro-amide is easily obtained. This, however, does not, by the methods used, lead to the desired amine. Nevertheless it is possible to obtain from the amide an impure bromo-amide (probably a mono-bromo-amide). The latter compound, when rearranged in alcoholic solution with sodium ethylate,⁸ yields in solution an intermediate product, probably the urethan, which upon acid hydrolysis gives β -triphenylethylamine. Analyses of the amine and its hydrochloride, chloroplati-

⁴ The latter observation is of theoretical interest. Violent reduction results, as noted, exclusively in the rupture of the carbon-carbon bond; this suggests that triphenyl acetonitrile may be minimally iodized in alcoholic solution into triphenylmethyl ion and cyanide ion.

⁵ A recent paper by Rupe and Gisiger [*Helv. Chim. Acta* [4] 8, 343 (1925)] describes the reduction of triphenyl acetonitrile by means of hydrogen in the presence of catalytic nickel. The results of this experiment were somewhat uncertain since 15 g. of the nitrile yielded only 0.1 to 0.2 g. of a hydrochloride, the melting point of which was stated to be 214° (m. p. of β -triphenylethylamine hydrochloride observed in the present work, $239\text{--}240^\circ$).

⁶ Henderson, *J. Chem. Soc.*, 51, 226 (1887).

⁷ Fosse, *Compt. rend.*, 145, 197 (1907).

⁸ This procedure is based upon that of Lengfeld and Stieglitz, *Am. Chem. J.*, 16, 370 (1894).

nate, benzoyl derivative and ethyl urethan derivative establish the identity of the compound. The melting point of the amine is 132° as compared with 116° reported by Elbs for his product. Curiously, the nitrate of β -triphenylethylamine is rather difficultly soluble in water.

Because of the unsatisfactory yields given by the bromo-amide procedure, it was deemed valuable to study the preparation of the amine starting with the hydroxamic acid derivative. For this purpose the benzoyl derivative of β -triphenylpropionhydroxamic acid, $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHOCOC}_6\text{H}_5$, was synthesized. When this substance is dropped upon a hot aqueous solution of alkali it is practically quantitatively rearranged, yielding β -triphenylethylamine and *sym*.-di- β -triphenylethylurea, $[(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{NH}]_2\text{CO}$. The urea is the chief product of the reaction. From it β -triphenylethylamine is easily obtained in good yield by means of hydrolysis under pressure with alcoholic hydrochloric acid. The relationship of the urea to the amine is further established from the observation that the former compound is produced by the action of phosgene upon the amine.

Experimental Part

Preparation of β -Triphenylpropionic Acid

(A) **By Henderson's Method.**⁶—As stated earlier in the paper, the yields obtained by this method (of the order of 5–10%) were inadequate for the preparation of the considerable quantity of acid required for this work.

(B) **By the Condensation of Cyano-ethyl Acetate and Triphenylbromomethane.**—When sodiocyano-ethyl acetate (suspended in either alcohol or ether) was treated with triphenylbromomethane under conditions similar to those described by Henderson for the analogous operation with sodiodiethyl malonate, the ultimate product was found to consist of yellow needles, probably cyanotriphenylmethylethylacetate, $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOC}_2\text{H}_5$, m. p. $215\text{--}216^{\circ}$, in very poor yield. The product resisted hydrolysis with 50% sulfuric acid at the boiling point of the acid. Because of the low yields no further attempts were made to hydrolyze the product and the method was abandoned for the preparation of β -triphenylpropionic acid.

(C) **By the Method of Fosse.**—Since Fosse⁷ does not give detailed directions for his preparation of β -triphenylpropionic acid, the following procedure which was found to give excellent results in this work is submitted.

Triphenylcarbinol, 100 g., is intimately mixed in a round-bottomed flask with malonic acid, 65 g. The mixture is heated in an oil-bath, at first *cautiously* at $140\text{--}150^{\circ}$, and is maintained within that temperature range until the first vigorous evolution of gas has subsided somewhat. The temperature is then brought to 160° and is maintained there for three hours. The melt is transferred to a beaker and treated with an

excess of sodium hydroxide, and about 1.5 liters of water. The mixture is heated in order to hasten solution and unchanged (almost pure) triphenylcarbinol is removed by filtration of the hot mixture. The cooled filtrate is treated with an excess of hydrochloric acid; β -triphenylpropionic acid precipitates,—usually in perfectly pure condition; the yield varies, 65 to 75 g.

β -Triphenylpropionamide, $(C_6H_5)_3CCH_2CONH_2$.—When β -triphenylpropionic acid (1 mole) is treated with pure thionyl chloride (3 moles), reaction readily takes place in the cold. The action is completed by means of heating just below the boiling point. The solution is allowed to cool slowly, when the acid chloride precipitates in beautifully crystalline form. It is removed by filtration and dried in a vacuum over sodium hydroxide. More may be obtained by means of evaporation of the filtrate at room temperature in a vacuum desiccator over sodium hydroxide; yield, excellent; m. p. of crude product, 132° . The crude product is now cautiously added to a well-agitated, concentrated solution of ammonia. The mixture is heated and is allowed to boil for several minutes; it is then cooled and the solid product, after careful trituration with water, is dried and crystallized two or three times from alcohol. The amide crystallizes from alcohol in white, plate-like crystals, sometimes cubical, resembling sodium chloride in form. It is soluble in benzene, acetone and other common organic solvents; m. p., 192° (corr.).

*Anal.*⁹ Subs., 0.3102 N, 12.8 cc. (over 50% KOH; 21° , 749.0 mm.). Calcd. for $C_{21}H_{19}ON$: N, 4.65. Found. 4.63.

N-Dichloro- β -Triphenylpropionamide, $(C_6H_5)_3CCH_2CONCl_2$.—This was obtained in slightly impure form when β -triphenylpropionamide, 4.5 g., was dissolved in 300 cc. of ethyl alcohol, treated at 5° with a concentrated solution of sodium hypochlorite (prepared from a solution of 15 g. of sodium carbonate and the calculated quantity of chlorine at -5°) and to the resulting solution chlorine water (saturated) was added little by little until a permanent precipitate was obtained. It was collected at once, washed with ice-cold chlorine water and dried in a vacuum over phosphorus pentoxide. The crude product melted at 116° ; when purification was attempted by means of crystallization from chloroform and ligroin, the melting point dropped 13° and the active chlorine content decreased 0.6%.

Anal. Subs., 0.1192· 9.36 cc. of 0.1281 N $Na_2S_2O_3$. Calcd. for $C_{21}H_{19}ONCl_2$: Cl, 10.6. Calcd. for $C_{21}H_{17}ONCl_2$: 19.2. Found: 17.9.

When a portion of the dichloro-amide was heated, chlorine was evolved and the cooled product was a "glass" which seemed to contain no definite chemical individual capable of easy isolation. Only a negligible amount of primary amine salt could be obtained in solution by treatment of the "glass" with hot, dil. hydrochloric acid. Treatment of the chloro compound with soda lime or with sodium ethylate in absolute alcohol likewise failed to yield an amine (after treatment of the resulting mixture with acid). The behavior of this dichloro-amide will be investigated more fully at a later date. It is of interest that the dichloro-amide readily oxidizes cold ethyl alcohol to acetaldehyde; chlorine is evolved at the same time and the parent amide is easily obtainable from solution in pure form: $(C_6H_5)_3CCH_2CONCl_2 + CH_3CH_2OH \longrightarrow (C_6H_5)_3CCH_2CONH_2 + CH_3CHO + Cl_2$.

Preparation of an Impure N-Bromo-amide, $(C_6H_5)_3CCH_2CONHBr$ (?).—Because of the insolubility of β -triphenylpropionamide in water it was found not possible to prepare the corresponding N-bromo-amide

⁹ The writer acknowledges with pleasure the generous assistance rendered by Drs. Andrew M. Neff and T. L. McMeekin in connection with some of the analytical work recorded in this paper.

by the usual procedure for this type of compound. The directions which follow were found to give a product which, when subjected to rearrangement by the Lengfeld-Stieglitz method,⁸ led to β -triphenylethylamine. The bromo-amide mixtures from successive preparations based on these directions were by no means uniform, varying in active bromine content from 9.1% to 13.0%; calcd. for $C_{21}H_{18}ONBr$: Br, 21.0.

To 3 g. of β -triphenylpropionamide dissolved in 200 cc. of ethyl alcohol and cooled to 0°, was added a ten-fold excess of potassium hypobromite in concentrated solution (prepared at -5°). Bromine water at 0° was added at once to precipitate the bromo-amide. This was collected, rapidly freed from mother-liquor, washed with cold bromine water and dried in a vacuum over phosphorus pentoxide. The product, a white powder, was found to be very reactive with hydriodic acid and with other reducing agents.

Rearrangement.—The crude bromo-amide was added to a solution of sodium ethylate (prepared from 1.3 g. of sodium) in 50 cc. of dry ethyl alcohol. The solution was boiled for three quarters of an hour, when a test proved that active bromine was absent. The solvent was allowed to evaporate on a water-bath. The residual viscous mass was washed with water, dissolved in a boiling mixture consisting of 200 cc. of alcohol, and 150 cc. of concd. aqueous hydrochloric acid, and the boiling was continued for five hours. The solvents were then allowed to evaporate; the residue was treated with hot water and the mixture filtered. When sodium hydroxide solution was added to the cooled filtrate a white precipitate resulted. This was taken up in ether, recovered by distillation of the ether, treated with a little concd. hydrochloric acid and the acid mixture was evaporated to dryness. The residual white needles were purified by dissolving in absolute alcohol and reprecipitating with dry ether. A mat of finely twined needles resulted, m. p., 239–240°. Analysis indicated that the product was β -triphenylethylamine hydrochloride. The hydrochloride is moderately soluble in alcohol and in water.

Anal. (Volhard) Calcd. for $C_{20}H_{18}NCl$: Cl, 11.4. Found: 11.5.

β -Triphenylethylamine, $(C_6H_5)_3CCH_2NH_2$.—The hydrochloride, prepared as described in the preceding section, is identical with that obtained after rearrangement of the benzoyl derivative of β -triphenylpropionhydroxamic acid (see below). The free amine was prepared directly in pure condition by adding a small excess of concd. ammonia water to an aqueous solution of the hydrochloride. The precipitate which resulted was collected, washed with water and dried. When viewed under the microscope it was found to consist of crystals which may be described simply but inadequately as elongated hexagonal platelets; m. p., 132° (corr.). When the amine is crystallized from ligroin (purified, b. p. 60–80°) the melting point does not change; the crystal form likewise is unchanged. The amine is soluble in hot ligroin, cold ether and benzene, moderately soluble in acetone and ethyl alcohol, and almost insoluble in water. It gives, with chloroform and potassium hydroxide, the carbylamine reaction.

Anal. Subs., 0.0695 N, 3.1 cc. (over 50% KOH; 20°, 755 mm.). Calcd for $C_{20}H_{19}N$: N, 5.1. Found: 5.0.

SALTS OF THE AMINE—The hydrochloride has already been described (see above). The dichromate (?) precipitates when a solution of a soluble dichromate is added to a solution of amine hydrochloride. The nitrate comes down in very characteristic manner when aqueous solutions of the hydrochloride and nitric acid are mixed. Under the microscope the salt is seen to consist of thin, elongated hexagonal plates. The salt may be crystallized from alcohol; decomposition point, 237°. Its solubility in water at 20° is approximately of the order 1:1000. None of the following ions, chlorate, perchlorate, oxalate, sulfate, interferes with the precipitation of the nitrate. Analysis and more complete solubility data will be submitted later.

CHLOROPLATINATE, $[(C_6H_5)_3CCH_2NH_2]_2PtCl_6$.—When a small excess of chloroplatinic acid solution is added to β -triphenylethylamine hydrochloride dissolved in a small volume of absolute alcohol, the chloroplatinate soon precipitates in yellow-orange crystals, which have the appearance of rhomboids under the microscope; m. p., 183° , with decomposition.

Anal. Subs., 0.1598: Pt, 0.0317. Calcd. for $C_{46}H_{40}PtCl_6$: Pt, 20.41. Found: 19.84.

BENZOYL DERIVATIVE, $(C_6H_5)_3CCH_2NHCOC_6H_5$.—The benzoyl derivative is formed when some β -triphenylethylamine hydrochloride in aqueous solution is shaken with a slight excess of benzoyl chloride in the presence of an excess of sodium carbonate. The product, a solid, is washed with water and crystallized from ethyl alcohol (platelets); m. p., 157.0° (corr.).

Anal. (Micro-Kjeldahl).¹⁰ Calcd. for $C_{27}H_{23}ON$: N, 3.7. Found: 3.6, 3.6.

URETHAN, $(C_6H_5)_3CCH_2NHCOOC_2H_5$.—This is formed when some β -triphenylethylamine is shaken with a small excess of ethyl chlorocarbonate in the presence of an excess of sodium carbonate. When all of the chlorocarbonate has been decomposed (with the aid of sodium hydroxide solution, if necessary) the urethan is taken up with ether, dried with sodium sulfate, recovered by evaporation of the ether, and crystallized from ligroin (b. p., $60-80^\circ$); m. p., 94° .

Anal. (Micro-Kjeldahl). Calcd. for $C_{23}H_{23}O_2N$: N, 4.1. Found: 4.2.

Preparation of β -Triphenylpropionhydroxamic Acid, $(C_6H_5)_3CCH_2CONHOH$.¹¹—A solution of 8 g. of crude β -triphenylpropionyl chloride (see section on preparation of β -triphenylpropionamide, above) in 100 cc. of ether is treated with 2.65 g. of sodium carbonate (anhydrous) and 1.75 g. of hydroxylamine hydrochloride. About 7 cc. of water is added and the mixture is shaken violently until all action has ceased (care: carbon dioxide is evolved). The solid product is brought upon a filter and washed with a little ether; it is thoroughly digested with hot water (to remove inorganic impurities), collected, and dried in a vacuum. The product so obtained is almost pure β -triphenylpropionhydroxamic acid; yield, 90%. It may be crystallized from ethyl acetate. The substance melts and decomposes at 182.5° ; it is readily soluble in alcohol, acetone, hot ethyl acetate and hot benzene; it is not soluble in ligroin. It gives, in alcohol solution, the usual color reaction with ferric chloride.

Anal. (Kjeldahl). Calcd. for $C_{31}H_{29}O_2N$: N, 4.42. Found: 4.23.

BENZOYL DERIVATIVE, $(C_6H_5)_3CCH_2CONHOCOC_6H_5$.—To a portion of the hydroxamic acid (the "crude" product may be used) to which has been added a small excess of 5% potassium hydroxide solution, is added slightly more than an equivalent amount of benzoyl chloride. The mixture is shaken vigorously. Suspended solid matter must be maintained in finely divided form or the benzylation will not be complete. When reaction is complete, potassium hydroxide solution is added, if necessary, until the small quantity of benzoic acid which floats near the surface is just dissolved. The product is collected, washed with water, dried and crystallized from alcohol; m. p., 171.5° ; yield, almost quantitative. The substance gives no color reaction with ferric chloride.

Anal. (Kjeldahl). Calcd. for $C_{33}H_{31}O_4N$: N, 3.33. Found: 3.29.

Rearrangement of the Benzoyl Derivative: Preparation of β -Triphenylethylamine.—The uncrystallized benzoyl derivative prepared from 24 g. of β -triphenyl-

¹⁰ Koch and McMeekin, *THIS JOURNAL*, **46**, 2066 (1924).

¹¹ The method is similar to one of those recommended by Jones and his co-workers, *THIS JOURNAL*, **43**, 2430 (1921); **44**, 412 (1922).

propionhydroxamic acid was added slowly in finely divided form to a gently boiling solution of 190 g. of potassium hydroxide in 500 cc. of water contained in a 2-liter flask. A vigorous reaction took place, accompanied by change of the organic substance to a white, caked mass which floated upon the surface. The mixture was refluxed for 40 minutes, diluted somewhat, cooled and filtered. The residue was washed well with water and then stirred with hot hydrochloric acid. The acid mixture was filtered and the residual solid washed with water and dried at 100°. From the filtrate 2.5 g. of β -triphenylethylamine was obtained by the addition of an excess of aqueous ammonia. The amine, after being dried over potassium hydroxide in a vacuum was practically pure, as indicated by its melting point. Its identity with the product previously obtained by rearrangement of the bromo-amide derivative was further established by conversion to the hydrochloride and the benzoyl derivative.

Analysis and the properties of the residual solid (from the acid treatment; see above) indicated that it was sym.-di- β -triphenylethyl-urea, $[(C_6H_5)_2CCH_2NH]_2CO$. The yield of crude urea was practically that calculated; m. p., 216–218°. When twice crystallized from alcohol the substance was pure and consisted of clumps of long, slender needles; m. p., 218.5–219°. It readily dissolves in benzene from which it may be precipitated by the addition of ligroin. The urea is completely converted to the parent amine by the procedure outlined in the following section.

Anal. Calcd. for $C_{41}H_{36}ON_2$: N, 4.90. Found (Kjeldahl): 4.84, 4.97; (Micro-Kjeldahl) 5.0, 5.0.

Hydrolysis of the Urea.—In sealed Pyrex "bomb" tubes (length, about 58 cm.; internal diameter, 1.7 cm.) the urea (5 g.) is heated with a mixture of 10 cc. of hydrochloric acid (d., 1.18–1.19) and 10 cc. of ethanol (95%) for 12 hours at 150°. The mixture thus obtained is concentrated to remove alcohol, diluted with water and filtered. To the filtrate ammonia is carefully added. Just beyond the "neutral point" a small amount of slightly colored matter precipitates. This is almost pure β -triphenylethylamine. An excess of ammonia is then added; the amine precipitates as a white solid in practically pure form. It is collected and dried. For complete purification it is dissolved in dry ether and the solution is treated with hydrogen chloride. The precipitate is collected, washed with ether and dried. The salt is dissolved in water and ammonia is then added to precipitate the amine.

Formation of the Urea from the Amine.—Some β -triphenylethylamine was treated with an excess of a solution of phosgene in toluene. Reaction was completed and the excess of phosgene removed on the water-bath. Slightly more than the same amount of amine dissolved in benzene was added to the reaction mixture (which presumably contained β -triphenylethylcarbamyl chloride), the solvents were evaporated, and the residual solid was digested with dil. hydrochloric acid to remove the excess of amine. The white solid obtained by filtration of the acid mixture was washed well and dried. Its melting point was 218° and was not lowered by admixture with some di- β -triphenylethyl-urea obtained from rearrangement of the hydroxamic acid derivative.

Summary

1. The synthesis of β -triphenylethylamine has been accomplished by the rearrangement of the benzoyl derivative of β -triphenylpropionhydroxamic acid and also by the rearrangement of an N-bromo derivative of β -triphenylpropionamide. The properties of the amine and those of several derivatives have been described; the properties of the amine and its derivatives have been found to differ from those set forth by Elbs, who stated that he prepared the substance by the reduction of triphenyl-

aceto nitrile, a procedure which could not be confirmed in the present work.

2. Among other new compounds described in this work are β -triphenylpropionamide, β -triphenylpropionhydroxamic acid and its benzoyl derivative, and *sym.*-di- β -triphenylethyl-urea.

3. Detailed directions for the preparation of β -triphenylpropionic acid by the method of Fosse are submitted.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE OXIDATION OF COMPOUNDS POSSESSING THE PRIMARY AMINO GROUP. I. DIPHENYLMETHYLAMINE

BY LESLIE HELLERMAN AND AGNES GRAHAM SANDERS¹

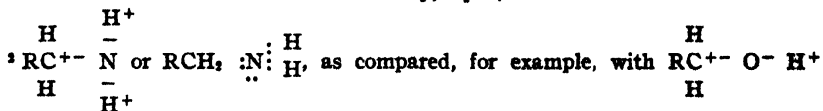
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The mechanism of oxidation of compounds possessing an amino group linked to a primary or secondary carbon atom (RCH_2NH_2 ; $\text{RR}'\text{CHNH}_2$) is a problem of considerable interest to organic chemists, and is also of importance in biological chemistry, particularly in connection with the important question of the oxidation of amino acids. Because of the electronic relationship of amino derivatives to hydroxylated compounds,² it has seemed interesting to inquire to what extent oxidation of amino compounds may, in general, produce substances of the types (that is, aldehydes and ketones as the ultimate products) which are obtained when the corresponding hydroxy derivatives are oxidized. From a theoretical point of view, the question of intermediate compounds formed during the course of an oxidation reaction is of additional importance.

Considerable work is recorded³ in which amino derivatives of types (1) RCH_2NH_2 , (2) $\text{RR}'\text{CHNH}_2$ and (3) $\text{RR}'\text{R}''\text{CNH}_2$ have been subjected to oxidation with agents related to hydrogen peroxide. Bases of the

¹ This preliminary paper is an abstract of part of a dissertation submitted to the University of Chicago by Agnes Graham Sanders, in partial fulfilment of the requirements for the degree of Master of Science, August, 1925. Presented before the Virginia Section of the American Chemical Society, April, 1926.



or $\text{RCH}_2 : \ddot{\text{O}} : \text{H}$. The valence sign $-$ as used here indicates the relative polarity of an atom resulting from the approach of a valence electron pair $:$, and the sign $+$ the corresponding polarity of the other atom held by the doublet bond.

³ (a) Bamberger and Seligman, *Ber.*, 36, 701 (1903). (b) Bamberger and Tschirner, *Ber.*, 32, 1675 (1899). For other references consult Houben-Weyl, "Methoden," Georg Thieme, Leipzig, 1922, vol. 2, p. 144.

tertiary type (Type 3 and the anilines) yield hydroxylamino derivatives in the first stage of oxidation. Hydroxylamines are undoubtedly also first formed when bases of Types 1 and 2 are oxidized, but in either of these cases the adjacent carbon atom is so readily attacked that the product of the second oxidation stage, an oxime, is the first which may be isolated. For example, $RR'CHNH_2 \rightarrow RR'CHNHOH \rightarrow RR'C=NOH$. The formation of the hydroxylamino derivative may be considered, in a sense, an oxidation of the nitrogen atom. The second step, which leads to the oxidation of the carbon atom linked to nitrogen, involves from the point of view of this paper the more fundamental change. The more active amines of Types 1 and 2 may yield a variety of products; an aldoxime, $RCH:NOH$, for example, which appears from oxidation of RCH_2NH_2 may evidently be further oxidized to the hydroxamic acid stage, since the aldehydo carbon atom still possesses a readily oxidizable position.⁴

Controlled oxidations of amines where the oxidizing agents were other than of the peroxide type have also been reported. Thus, uramil is oxidized to alloxan with great ease by the action of chlorine.^{5a, 6} Benzylamine is largely converted to benzaldehyde by the action of potassium permanganate.^{5b} The same amine, when oxidized with bromine in the presence of sodium ethylate in anhydrous alcoholic solution, yields a gummy product which may be completely hydrolyzed to benzaldehyde and benzonitrile.⁷ Aldehydes have been obtained by the action of oxygen in the presence of copper upon amino compounds.^{5c} Limitations of space prevent detailed discussion of these and other interesting examples.

In the present work, it seemed interesting to inquire what would be the ultimate product of oxidation when a substituted methylamine of high molecular weight is oxidized by bromine in the presence of sodium ethylate in anhydrous alcoholic solution. The amine selected for study was diphenylmethethylamine, $(C_6H_5)_2CHNH_2$.⁸ Bromine was chosen as the

⁴ According to the theory of Stieglitz, aldehydes and their addition products possess "exposed" electrons (readily lost to oxidizing agents) on the aldehydo carbon atom due chiefly to the labile character of the hydrogen atom. Compare Stieglitz, *THIS JOURNAL*, **44**, 1308 (1922); "Qualitative Chemical Analysis," The Century Co., New York, 1911, vol. 1, p. 291.

⁵ (a) Baeyer, *Ann.*, **131**, 298 (1864). (b) Goldschmidt and Voeth, *Ann.*, **435**, 265 (1924). (c) Traube and Schönewald, *Ber.*, **39**, 178 (1906).

⁶ See the discussion on p. 1745.

⁷ Hellerman, unpublished work.

⁸ Since the completion of this work and the writing of the paper Goldschmidt and Beuschel have reported [*Ann.*, **447**, 197 (1926)] the results of work on the oxidation of the same compound with permanganate in absolute acetone solution, the product of oxidation being iminobenzophenone. (Compare results reported in the present work.) These workers assume that the amine is "dehydrogenated" by the oxidizing agent, the resulting intermediate product, $(C_6H_5)_2CH.N<$, transforming itself to the imino compound.

oxidizing agent because it was considered that if the formation of a bromo-amine, $R_2CHNHBBr$, should constitute the first step in the oxidation series, we should have initially a situation comparable⁹ to that which obtains when amines are oxidized to oximes by means of Caro's acid. This distinction must, however, be noted: the hydroxylamines are *much more stable substances* than the bromo-amine derivatives. Anhydrous alcohol was selected as the reaction medium in order that hydrolysis of the bromo-amine derivative, if formed intermediately, might be practically entirely prevented.

As recorded in the experimental section, benzophenone in excellent yield was the ultimate product of the oxidation.^{8a} In order to attempt an elucidation of the nature of the change, it was postulated that the assumed initial product of reaction—the monobromo derivative of the amine, $(C_6H_5)_2CH.NHBBr$ —rearranges or undergoes intramolecular oxidation-reduction, yielding iminobenzophenone according to the equation $(C_6H_5)_2CH.NHBBr + NaOC_2H_5 \rightarrow (C_6H_5)_2C=NH + NaBr + C_2H_5OH$. This imine has been well described;¹⁰ water hydrolyzes it promptly to benzophenone and ammonia. This hydrolysis would constitute the final step in the assumed series of reactions leading from diphenylmethylamine to benzophenone.

In order to ascertain if such an hypothesis of reaction mechanism could be justified experimentally, the behavior of N-chlorodiphenylmethylamine, $(C_6H_5)_2CHNHCl$, in the presence of sodium ethylate in anhydrous alcoholic solution was observed. The N-chloro compound was used because N-chloro-amines stand close to N-bromo-amines chemically and are more easily synthesized than the latter. Its preparation was accomplished by treatment of a solution of the amine hydrochloride with a *neutral* solution of an equimolecular quantity of sodium hypochlorite. This chloro-amine was, in fact, found to resolve itself with great ease, under the conditions of experiment, into iminobenzophenone.

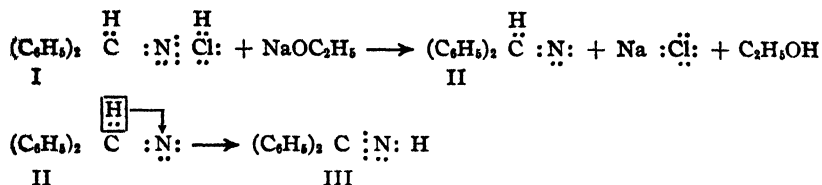
While it would appear undesirable to become committed at the present time to any complete interpretation of such a reaction, the change undoubtedly is related essentially to this fundamental fact: the carbon atom has become oxidized at the expense, ultimately, of the "positive" halogen atom, which has become reduced to halide ion. Such an intramolecular change might, for example, take place very much in the manner of the Hofmann rearrangement.¹¹ In terms of the more recent practices

⁹ Compare the many well-known chemical characteristics manifested in common by hydroxylamino derivatives, $RNHOH$, and halogeno-amines, $RNHX$.

¹⁰ Hantzsch and Kraft, *Ber.*, **24**, 3516 (1891). Moureu and Mignonac, *Compt. rend.*, **156**, 1801 (1913).

¹¹ Hofmann, *Ber.*, **14**, 2725 (1881). The formulation which follows is intimately related to the general theories of molecular rearrangements which have been advanced by Stieglitz and his collaborators. See *THIS JOURNAL*, **36**, 272 (1914); **38**, 2046 (1916) for references to the literature. Compare also Jones, *Am. Chem. J.*, **50**, 440 (1913).

of polarity expression we should have



Briefly stated, in the presence of the base sodium ethylate, $\text{H} + \text{Cl}-$ is removed from the nitrogen atom in compound I, the nitrogen atom being at the same time oxidized by virtue of the removal of an electron pair by $\text{Cl}:$. The unstable univalent nitrogen derivative II results (intermediately). The nitrogen atom in II now completes its octet by attracting $:\text{H}$ from the carbon atom. The loss of $:\text{H}$ by the carbon atom involves the oxidation of the latter and the whole process results in the formation of iminobenzophenone (III).

In spite of the significant result here obtained for the intramolecular oxidation-reduction of the chloro-amine derivative, it is not to be concluded that *direct* oxidation of amines of Types $\text{RR}'\text{CHNH}_2$ and RCH_2NH_2 with halogens or other oxidizing agents necessarily follows exclusively such a course as has been suggested. *Direct attack* at the carbon atom vicinal to the amino group is by no means excluded. Such a path must, indeed, be especially considered when such activating groups as phenyl (as in benzylamine and in the case under present study) or carbonyl (as in the case of uramil) are carried by the vicinal carbon atom; under such circumstances we should have characteristic labilization of hydrogen atoms carried by the carbon atom and the susceptibility of the latter to oxidation would be markedly enhanced.⁴ The subject will be discussed in greater detail in a later paper which will describe further work on the oxidation of amines of the type $\text{RR}'\text{CHNH}_2$, and of the secondary amines. Work is being continued also on substances of the type RCH_2NH_2 , particularly β -diphenylethylamine and β -triphenylethylamine, $(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{NH}_2$,¹² and on the oxidative mechanism of the α -amino acids, $\text{RCHNH}_2 \cdot \text{COOH}$.

Experimental Part

1. **Oxidation of Diphenylmethylamine.**—Diphenylmethylamine hydrochloride¹³ (5 g), dissolved in 50 cc. of anhydrous alcohol,¹⁴ was treated with an alcoholic solution of 3

¹² Hellerman, *THIS JOURNAL*, 49, 1735 (1927).

¹³ The melting point assigned to this compound in the literature [Leuckart and Bach, *Ber*, 19, 2130 (1886)] is 270° . It was found in the present work that the hydrochloride had not melted at 293° .

¹⁴ Prepared from commercial absolute alcohol by prolonged treatment with lime and careful distillation, care to prevent the introduction of moisture being exercised both in the preparation and storing of the alcohol.

equivalents of sodium ethylate, prepared by treatment of 1.57 g. of sodium with 50 cc. of anhydrous alcohol. With constant shaking, one equivalent of bromine (3.64 g.) was then quickly added; sodium halides precipitated at once. After the reaction mixture had been gently refluxed for half an hour, a test with hydriodic acid for active halogen failed, and the reaction was then considered complete. The solution was slightly acidified with dil. sulfuric acid, and the alcohol was removed by distillation with steam. The reaction product separated from the residual aqueous solution as a light yellow oil. This was extracted with ether and the ethereal extract dried. After evaporation of the ether an oil remained which, when cooled, promptly solidified to a mass of slightly colored, radiating prismatic crystals. The melting point was found to be 47° and was not depressed when the material was mixed with some known benzophenone. The identity of the product as benzophenone was thus established. Of the product, 2.72 g. was obtained (yield, 66%).¹⁵

2. Preparation of *N*-Monochlorodiphenylmethylamine, $(C_6H_5)_2CHNHCl$.—This compound was prepared by the action of the calculated amount of sodium hypochlorite upon a solution of diphenylmethylamine hydrochloride. An alkaline solution of sodium hypochlorite was prepared in the usual way by means of passing chlorine gas into an excess of sodium hydroxide solution at 0° . The active chlorine content of this solution was determined in the usual manner. The solution was analyzed for excess alkalinity by the procedure of Berg.¹⁶ Before use it was titrated for active chlorine, and the required quantity was then treated at 0° , as described by Berg, with the exact amount of standard acid necessary to neutralize the excess of alkali.

For the preparation of *N*-monochlorodiphenylmethylamine, diphenylmethylamine hydrochloride (5 g.) was dissolved in about 30 cc. of water, and to this was added at 5° a neutral solution of sodium hypochlorite containing exactly one molecule of the hypochlorite for each molecule of the amine salt. The mixture almost immediately became cloudy and very soon a pale yellow solid precipitated. This product was collected on a filter at once, washed with three small portions of cold chlorine water, and dried in a vacuum over phosphorus pentoxide. The substance was found to possess the properties characteristic of chloro-amine derivatives. The yield was almost quantitative.

Anal. Calcd for $C_{13}H_{11}NCl_2$: Cl, 28.15. Calcd. for $C_{13}H_{12}NCl$: Cl, 16.3. Found: 15.7, 15.9.

3. Intramolecular Oxidation-Reduction of *N*-Monochlorodiphenylmethylamine.—The chloro-amine (5 g.) was dissolved in 30 cc. of anhydrous alcohol and treated with an equimolecular quantity of sodium ethylate prepared by treatment of 0.52 g. of sodium with 50 cc. of anhydrous alcohol. The mixture was vigorously shaken. Precipitation of a solid (sodium chloride) began at once with the evolution of heat. The mixture was gently refluxed for five minutes. A test at this point for active halogen failed, and the reaction was considered complete. Care to prevent the introduction of moisture was exercised throughout the entire experiment. The alcohol was removed by distillation under reduced pressure (20 mm.). The residue consisted of a mixture of sodium chloride with a quantity of a yellow oil. The oil was found to be identical with iminobenzophenone, as proved in the succeeding section.

4. Isolation of Iminobenzophenone Hydrochloride, $(C_6H_5)_2C=NH_2Cl$.—The

¹⁵ When diaryl methylamines are oxidized under the conditions described in this section by either bromine or iodine, iminoketones have been found to be present in the reaction mixtures, easily isolated as hydrochlorides. Experimental details will be submitted later

¹⁶ Berg, *Ann. chim. phys.*, [7] 3, 289 (1894).

residual oil was extracted with anhydrous ether. The imino compound was next isolated in the form of its hydrochloride in the following manner. The ethereal solution was saturated with dry hydrogen chloride. A white precipitate resulted, which was brought upon a filter, washed with absolute ether, and dried in a vacuum in order to remove ether and traces of free hydrogen chloride. That the product was the hydrochloride of iminobenzophenone was indicated by analysis for chlorine by the Volhard method. The yield was 90% of that expected.

Anal. Calcd. for $C_{13}H_{11}NCl$: Cl, 16.30. Found: 16.43.

This analysis would not, of course, differentiate between the hydrochloride of iminobenzophenone and that of diphenylmethylamine, if present. The former compound may, however, be completely differentiated from the latter by its characteristic behavior when hydrolyzed with water.¹⁷ That the product was *completely hydrolyzed to benzophenone* when dissolved in water is demonstrated by the following. Of the hydrochloride, 1.5 g. was dissolved in 25 cc. of water. A clear solution resulted which almost immediately became milky. After several minutes' standing, it was found that droplets of an oil had collected. The reaction product was carefully extracted with ether. The extract was dried, and the ether was evaporated. A light yellow oil remained which crystallized when it was cooled. The melting point of the product was found to be 47.9° and that of a mixture with some benzophenone was also 47.9° . The recorded melting point of benzophenone is 48° . The yield, 1.2 g., was practically quantitative. A test of the aqueous solution after the ether extraction proved that chloride ion and ammonium ion were present.

Merely as an accessory test, some of the iminobenzophenone hydrochloride obtained in this work was added to a solution of hydroxylamine and sodium carbonate, and the mixture was treated in the manner customarily employed for the preparation of benzophenone oxime. An excellent yield of the pure oxime was obtained.

Summary

1. Some aspects of the problem of the mechanism of oxidation of amino derivatives of the types RCH_2NH_2 and $RR'CHNH_2$ are briefly discussed from the point of view of modern concepts of oxidation-reduction.
2. The oxidation of diphenylmethylamine in anhydrous alcoholic solution in the presence of sodium ethylate is shown to yield benzophenone as the chief product.
3. A mechanism of reaction to account for the product obtained and to elucidate the nature of the reaction is postulated; experimental work is presented which is considered, in a measure, to justify the proposed theory.
4. The conversion of N-monochlorodiphenylmethylamine into iminobenzophenone by means of an anhydrous alcoholic solution of sodium ethylate was accomplished.
5. The preparation of N-monochlorodiphenylmethylamine is described.

CHICAGO, ILLINOIS

¹⁷ See the theoretical part and the references cited there.

[CONTRIBUTION FROM THE GOODYEAR TIRE AND RUBBER COMPANY]

RESEARCHES ON MERCAPTOTHIAZOLES. I

BY JAN TEPPEMA AND L. B. SEBRELL

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Introduction

Since the discovery of 2-mercaptobenzothiazole by Hofmann,¹ who prepared this compound from *o*-amidothiophenol and carbon disulfide, further research on this compound and its possible derivatives was desirable when its value as an accelerator of rubber vulcanization was discovered.

The synthesis of 2-mercaptobenzothiazole from aniline, sulfur and carbon disulfide² not only offered a commercial preparation but made it possible to prepare several derivatives, using a substituted aniline according to the same method. This method, however, is limited in its application, as only six substituted 2-mercaptobenzothiazoles could be prepared. Another disadvantage is the necessity of carrying out the reaction in a closed system whereby pressures as high as 1000 lbs. per sq. in. (7.03×10^5 g./sq. cm.) were obtained.

For laboratory use it seemed very desirable to develop a simple method of preparing 2-mercaptobenzothiazole which could be extended to several new derivatives. The present paper outlines a method of preparing 2-mercaptobenzothiazole in one step from *o*-nitrochlorobenzol, a comparatively cheap material. The method is capable of extension to the preparation of other derivatives such as the halogen, amido and carboxyl derivatives from the corresponding *o*-nitrochlorobenzol derivatives. It has been shown by Blanksma³ that *o*-nitrochlorobenzol reacts easily with sodium disulfide to give dinitrodiphenyl disulfide.

Bogert and Snell⁴ have developed a method for the reduction of this disulfide using zinc and acetic acid, resulting in the formation of the zinc salt of *o*-amidothiophenol, from which Bogert and his co-workers have prepared a large number of phenylbenzothiazoles. From the zinc salt of *o*-amidothiophenol the diaminodiphenyl disulfide was obtained by passing air through its ammonia solution. The best yield obtained by Bogert and by ourselves is approximately 65–75%; the isolation of the pure material is tedious and the loss through crystallization large.

It has been found that the alkaline hydrosulfides are efficient reducing agents for dinitrodiphenyl disulfide, giving a good yield of the corresponding diamino compound.

Several examples are described in the literature whereby alkali hydro-

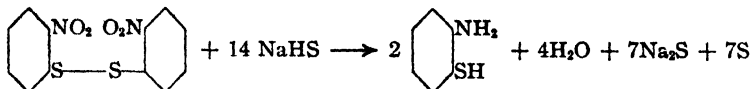
¹ Hofmann, *Ber.*, **20**, 1788 (1887).

² Sebrell and Boord, *THIS JOURNAL*, **45**, 2396 (1923).

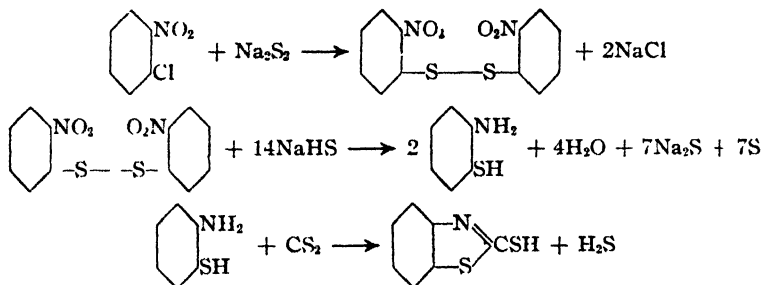
³ Blanksma, *Rec. trav. chim.*, **20**, 121 (1901).

⁴ Bogert and Snell, *THIS JOURNAL*, **46**, 1308 (1924).

sulfides are used for the reduction of the nitro compounds to the corresponding amino compounds⁵ and usually the reaction can be accomplished in water solution when the final product is soluble in alkali. In our case the reduction scheme is represented by the following reaction.



Instead of alkali hydrosulfides, sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$, can be used, either alone in alcohol, or in water solution in the presence of alkali. The third step in the preparation of 2-mercaptobenzothiazole from *o*-nitrochlorobenzol is the interaction of carbon disulfide with *o*-aminothiophenol. Hofmann obtained it by refluxing *o*-aminophenyl mercaptan with carbon disulfide for 12–14 hours. No data about yields are given, so that the reaction was carried out for the same length of time with *o*-diaminodiphenyl disulfide, giving a low yield of 2-mercaptobenzothiazole. Considering the three reaction schemes by which 2-mercaptobenzothiazole is formed from *o*-nitrochlorobenzol,



it occurred to us that these reactions could be accomplished in one step.

It is known that sodium sulfide solutions absorb carbon disulfide, forming trithiocarbonates, which decompose on heating,⁶



so we may assume that also in the case of sodium hydrosulfide we have the reaction,



and as sodium sulfide is always present in a sodium hydrosulfide solution, Reactions 1 and 2 must take place simultaneously.

This shows that carbon disulfide is converted into a water-soluble trithiocarbonate, which will give carbon disulfide in the nascent and more reactive form.

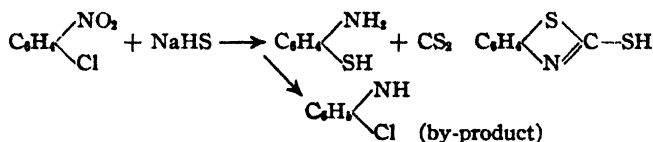
Another factor that facilitates the formation of 2-mercaptobenzothiazole from diaminodiphenyl disulfide is the use of hydrogen sulfide for the formation of sodium hydrosulfide from sodium sulfide throughout the re-

⁵ Teppema, *Rec. trav. chim.*, **42**, 40 (1923).

⁶ Victor Meyer and Jacobson, *Org. Chem.*, I (2), 1367.

action, whereby the free *o*-amino thiophenol will be present instead of the corresponding disulfide. Experiments confirmed this theory.

It was also possible to combine Reaction 1 with 2 and 3. Blanksma⁷ and Wohlfahrt⁸ state that by the action of sodium disulfide on *o*-nitrochlorobenzol, some *o*-chloro-aniline is formed, and the best yield of dinitrodiphenyl disulfide obtained by ourselves did not exceed 75%. Several modifications in the reactions either cut down or did not affect the yield of final product. To eliminate the loss caused by the reducing action of sodium disulfide on an alcoholic solution of *o*-nitrochlorobenzol, the three reactions were carried out in one step from *o*-nitrochlorobenzol, sodium hydrosulfide and carbon disulfide. The result was an 87.5% yield of 2-mercaptobenzothiazole, based on the *o*-nitrochlorobenzol used; m. p. of the crude material, 173–174°. One crystallization from alcohol gave needles; m. p., 177–178°. The combined reactions may be represented as follows.



As already mentioned, substituted 1-chloro-2-nitrobenzol compounds can be used as starting material. The yields are best for the halogen derivatives. The nine following substituted 2-mercaptobenzothiazoles were prepared according to the method described: 5-chloro-2-mercaptobenzothiazole, 5-bromo-2-mercaptobenzothiazole, 2-mercaptobenzothiazole-5-sulfonic acid (sodium salt), 5-amido-2-mercaptobenzothiazole, 7-methyl-2-mercaptobenzothiazole, 5-methyl-2-mercaptobenzothiazole, 2-mercaptobenzothiazole-5-carboxylic acid, 2-mercaptobenzothiazole-4-carboxylic acid and 2-mercapto-5-oxybenzothiazole.

The combined reaction could not be applied in all cases, as will be shown in the Experimental Part.

Attempts to prepare dichloro-substituted 2-mercaptobenzothiazoles from the corresponding nitrotrichlorobenzois failed and the constitution of the resulting compounds is still in doubt.

The melting points given in this work are all uncorrected. However, they were all made with the same thermometer under identical conditions.

Experimental Part

(a) **Alkali Hydrosulfide Reduction. 2-2'-Diaminodiphenyl Disulfide (Reaction 2).**—A mixture of 5 g. of 2,2'-dinitrodiphenyl disulfide, 150 cc. of water and 30 cc of concd. aqueous ammonia was saturated with hydrogen sulfide and then heated under reflux for two hours. To the solution was added another 30 cc. of concd. aqueous ammonia and it was again saturated with hydrogen sulfide. After refluxing for two

⁷ Blanksma, *Rec. trav. chim.*, **28**, 108 (1909).

⁸ Wohlfahrt, *J. prakt. Chem.*, [2] **66**, 553 (1902).

hours more, the solution was acidified with hydrochloric acid and evaporated on a steam-bath until all of the sulfur had coagulated and a clear solution was obtained. The solution was filtered hot and the residue washed with hot water. The filtrate contains the reduction product, mostly in the form of the hydrochloride of the mercaptan. To oxidize this to the disulfide, two methods were applied.

(1) The acid solution was neutralized by a sodium carbonate solution and air was drawn through the solution to oxidize the free mercaptan to the disulfide.

(2) An alcoholic solution of iodine was added to the acid solution until the iodine color remained. The solution was filtered and the filtrate neutralized with sodium carbonate. The yield of the first product of the diamido compound was 3.9 g.; m. p., 75–80°. Redissolving in hydrochloric acid solution, boiling with charcoal and reprecipitating with sodium carbonate gave 3.4 g.; m. p., 80°. According to the literature, the melting point of the *o*-diaminodiphenyl disulfide is 93°. As another purification of the obtained product by redissolving in hydrochloric acid and reprecipitating with sodium carbonate did not raise the melting point, a sulfur analysis was made

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: S, 26.68. Found: 25.81.

Once recrystallized from dilute alcohol the melting point was 87°. Twenty-five g. of crude product gave 20 g. by recrystallization from dilute alcohol.

Instead of ammonium hydrosulfide, sodium hydrosulfide could be used. With the same procedure, 10 g. of *o*-dinitrodiphenyl disulfide gave 7.6 g. of *o*-diaminodiphenyl disulfide. This product was redissolved in hydrochloric acid, charcoal added, and the solution refluxed for two hours. Reprecipitation gave 7.2 g. of *o*-diaminodiphenyl disulfide; m. p., 80–85°. Recrystallization from dilute alcohol gave 5.5 g. of 2,2'-diaminodiphenyl disulfide; m. p., 87°.

(b) **Reduction with Sodium Hydrosulfite.**—A mixture of 10 g. of *o*-dinitrodiphenyl disulfide and 150 cc. of alcohol was boiled under reflux, and to the hot solution 50 g. of sodium hydrosulfite was added in portions, through the condenser. At each addition 5–10 cc. of water was added; total addition time, one hour; total added water, 100 cc. After two hours' more heating the solution was filtered and the residue (inorganic salts) washed with hot alcohol. The filtrate was acidified and evaporated until dry. The residue was treated with hydrochloric acid and filtered hot. A small amount of tar remained on the filter. The filtrate was rather dark colored and was boiled with charcoal for two hours. After filtering and cooling, the solution was neutralized with sodium carbonate; first product, 8 g.; m. p., 70–75°. Once reprecipitated 7 g. was obtained. Five g. of *o*-diaminodiphenyl disulfide was obtained by recrystallization from dilute alcohol; m. p., 87°.

The reduction of the *o*-dinitrodiphenyl disulfide could also be accomplished by sodium hydrosulfite in water solution if a small amount of alkali was added to increase the solubility of the final product. The melting points given for the *o*-diaminodiphenyl disulfide, that is, 87°, are lower than those usually given for this compound. However, material of this purity was entirely suitable for use in other reactions described later in this paper. Small samples on further recrystallization showed a melting point of 92–93°, but the loss on crystallization is high.⁴

Reaction of *o*-Diaminodiphenyl Disulfide and Carbon Disulfide (Reaction 3).—Five g. of *o*-diaminodiphenyl disulfide, m. p. 87°, and 30 cc. of carbon disulfide were refluxed for 15 hours and carbon disulfide was evaporated on the water-bath. The residue was acidified with hydrochloric acid and filtered hot.

Neutralization with sodium carbonate gave 3 g. of unchanged *o*-diaminodiphenyl disulfide. The residue on the filter was heated with hot, dilute, aqueous ammonia and filtered. A small amount of black tar (sulfur) was left. Filtrate treated with hydrochloric acid gave 2 g. of mercaptobenzothiazole; yield, 32%.

Reduction with Ammonium Hydrosulfide with Carbon Disulfide Present.—A mixture of 5 g. of *o*-dinitrodiphenyl disulfide, 200 cc. of water and 30 cc. of concd. aqueous ammonia was saturated with hydrogen sulfide previously passed through a wash bottle containing water and carbon disulfide. The solution was boiled under reflux at the same time for two hours. After this, the heating was stopped, 30 cc. of concd. aqueous ammonia was added and hydrogen sulfide again bubbled through until the mixture had cooled to room temperature. The mixture was then refluxed again for two hours.

The dark red solution was acidified and evaporated until the sulfur had coagulated and a clear solution was obtained. The white precipitate was filtered and extracted twice with hot aqueous ammonia. Precipitation with hydrochloric acid gave 5.2 g. of mercaptobenzothiazole; m. p., 176°; yield, 96%. The residue on the filter proved to be pure sulfur; m. p., 118°.

Reduction with Sodium Hydrosulfide in the Presence of Carbon Disulfide.—The procedure followed was the same as in the case of ammonium hydrosulfide. Twenty-five g. of sodium sulfide was used instead of ammonia. The advantage of this method lies in the fact that sodium sulfide is regenerated from the sodium hydrosulfide, while in the case of ammonium hydrosulfide the ammonia escapes, forming crystals of ammonium hydrosulfide in the condenser. The yield of mercaptobenzothiazole was identical with the yield obtained above.

In the case of the sodium hydrosulfite reduction the two reactions could not be combined in water solution. Addition of carbon disulfide to the alcoholic solution with sodium hydrosulfite gave a very small amount of mercaptobenzothiazole after a long time of heating. This fact led to the assumption that the easy way in which carbon disulfide reacts in the sodium hydrosulfide reduction method must be explained by the formation of a water-soluble carbon disulfide compound, which decomposes on heating to give carbon disulfide in the nascent state. This assumption is verified by the following experiments.

(a) Five g. of *o*-diamidodiphenyl disulfide and 30 cc. of carbon disulfide were refluxed for 6.5 hrs. The excess of carbon disulfide was evaporated and the residue treated with hot dil. hydrochloric acid to extract unchanged *o*-diamidodiphenyl disulfide. The residue, a mixture of mercaptobenzothiazole and sulfur, was extracted with hot dil. aqueous ammonia and the extract precipitated with hydrochloric acid; yield, 0.5 g.

(b) Five g. of *o*-diamidodiphenyl disulfide, 50 cc. of water and 9 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were saturated with hydrogen sulfide, the latter previously having been passed through a wash bottle containing water and carbon disulfide. After 6.5 hours' reaction, the solution was cooled and acidified with hydrochloric acid, evaporated until the sulfur had coagulated completely, and filtered hot.

The filtrate did not give a precipitate with sodium carbonate solution, an indication that no unchanged *o*-diamidodiphenyl disulfide remained. The residue on the filter was extracted with hot, dilute, aqueous ammonia and precipitated with hydrochloric acid. Six and one-tenth g. of mercaptobenzothiazole was obtained; yield, 98%.

The difference between Expts. (a) and (b) is that in Expt. (b) both carbon disulfide and *o*-amidothiophenol are formed in the nascent state. In

Expt. (a) the free *o*-aminothiophenol is probably formed as an intermediate product.

After a further study it did not appear that the above experiments were sufficiently conclusive since in Expt. a the disulfide must undergo reduction to the free mercaptan before it can react with carbon disulfide.

To prove further the validity of the previous conclusions the following experiments were carried out.

(c) Five g. of *o*-aminothiophenol was refluxed with 25 cc. of carbon disulfide for six hours. After this the carbon disulfide was evaporated and the residual liquid treated with dil. hydrochloric acid. No residue remained after heating on a water-bath.

It seems, therefore, that *o*-aminothiophenol as such reacts very slowly with carbon disulfide. Hofmann claims that 2-mercaptobenzothiazole is formed after 24 hours' refluxing but does not mention the yield obtained.

(d) Five g. of *o*-aminothiophenol and 2 g. of sodium hydroxide were mixed with 50 cc. of water. Carbon dioxide, which had been saturated with carbon disulfide, was bubbled through the mixture, which was then refluxed for six hours. Acidification gave 6 g. of 2-mercaptobenzothiazole (98%). These experiments show that either *o*-aminothiophenol or carbon disulfide in the nascent state causes a complete reaction within reasonable time.

We are thus unable to say definitely that the success of our new method for making 2-mercaptobenzothiazole is entirely dependent upon the formation of nascent carbon disulfide from sodium trithiocarbonate. However, it may be equally dependent upon the presence of nascent *o*-aminothiophenol formed by the action of hydrogen sulfide on the sodium salt.

Combination Reactions 1, 2 and 3.—A solution of 250 g. of $\text{Na}_2\text{S}\cdot 8\text{H}_2\text{O}$ in 1 liter of water was saturated with hydrogen sulfide, the latter previously having been passed through a wash bottle containing water and carbon disulfide. After complete saturation, 100 g. of *o*-nitrochlorobenzol was added and the mixture refluxed for 20 hours on a sand-bath, while hydrogen sulfide saturated with carbon disulfide was bubbled through the solution. It is essential that in the beginning of the reaction the mixture be not heated too strongly. After the reaction was complete, a dark red solution was obtained. The reaction mixture was steam-distilled and the steam distillate extracted with ether. The ether solution was dried over anhydrous potassium carbonate and gave 8.5 g. of *o*-chloro-aniline; b. p., 207°. If the reaction were not carried out to completion, the *o*-chloro-aniline was mixed with unchanged *o*-chloronitrobenzene. These could be separated by extracting the *o*-chloronitrobenzene from the acid-water mixture. The residual water solution was made alkaline and again ether-extracted.

The alkaline residue of the steam distillation was acidified with hydrochloric acid and evaporated until all of the sulfur had coagulated and a clear solution was obtained.

The precipitate, consisting of sulfur and mercaptobenzothiazole, was twice extracted with warm aqueous ammonia and reprecipitated with hydrochloric acid. The water filtrates were concentrated to regain the water-soluble mercaptobenzothiazole; total yield, 92.5 g., or 87.5%.

A modification of this experiment was made by using alcohol as a solvent instead of water. The yield was only 73.5% and the product darker colored than in the reaction where water was used.

If commercial *o*-nitrochlorobenzol (containing a small amount of the *para* derivative) was used, the yield of 2-mercaptobenzothiazole was 84%. The procedure

outlined above was followed in the synthesis of the derivatives of 2-mercaptobenzothiazoles described in this paper, where reference is made to the general procedure.

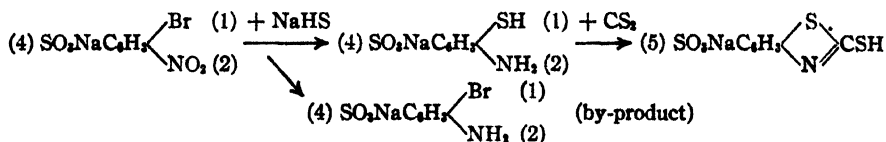
5-Chloro-2-mercaptobenzothiazole.—Following the same procedure as described for 2-mercaptobenzothiazole, a yield of 87% of 5-chloro-2-mercaptobenzothiazole was obtained. From 250 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dissolved in 500 cc. of water, hydrogen sulfide, carbon disulfide and 100 g. of 1,4-dichloro-2-nitrobenzol, reacted for 20 hours, 91 g. of 5-chloro-2-mercaptobenzothiazole was obtained.

This compound, not previously mentioned in the literature, has an enormous absorption capacity for water and alcohol when first precipitated from these solutions. The best way to obtain it in a dry state is to press it out in a piece of fine-woven cloth. After drying, it was crystallized from alcohol, giving colorless needles; m. p., 192° .

Anal. Calcd. for $\text{C}_7\text{H}_4\text{NS}_2\text{Cl}$: Cl, 17.60; N, 6.94. Found: Cl, 17.18; N, 6.98.

Pressure Reactions.—If the reaction was carried out under pressure, the time for complete reaction was shortened noticeably, but the highest yield obtained did not exceed 62%.

2-Mercaptobenzothiazole-5-sulfonic Acid (Sodium Salt).—This compound was prepared successfully from 2-nitrobromobenzol-4-sulfonic acid. The reaction scheme is as follows.



The reaction product, consisting of sulfur and the sodium salt of 2-mercaptobenzothiazole-5-sulfonic acid, was extracted with boiling alcohol, leaving most of the sulfur behind.

One hundred g. of 2-nitro-1-bromobenzol-4-sulfonic acid gave 70 g. of small, white needles. This material was purified by crystallizing it twice from boiling water, whereby most of the alcohol-soluble sulfur is left behind.

Anal. Calcd. for $\text{C}_7\text{H}_4\text{O}_2\text{NS}_2\text{Na}$: S, 35.68; N, 5.20; Na, 8.55. Found: S, 35.86; N, 4.82; Na, 8.0.

This compound is quite soluble in water and hot alcohol, insoluble in ether, benzene and chloroform.

Properties.—(a) A solution of the sodium salt of 2-mercaptobenzothiazole-sulfonic acid in alcohol gives a precipitate with iodine, proving its nature as a mercaptan.

In water solution no precipitate is formed by the addition of iodine, showing that the sodium salt of the acid is soluble in water.

(b) A water solution of the sodium salt treated with zinc acetate does not give a precipitate. On evaporation to a smaller volume, the unchanged sodium salt is recovered.

(c) A water solution of the sodium salt treated with a water solution of the equivalent amount of lead acetate gave an instantaneous color change to yellow, which disappeared quickly with the formation of a colorless precipitate.

This was filtered, washed with water and dried.

Anal. Calcd. for $\text{C}_7\text{H}_4\text{O}_2\text{NS}_2\text{Pb}$: Pb, 45.80. Found: Pb, 43.66.

5-Amido-2-mercaptobenzothiazole.—The preparation of this compound from 1-chloro-2,4-dinitrobenzol or 2,4-tetranitrodiphenyl disulfide with sodium hydrosulfide and carbon disulfide was not successful.

Forty-five g. of 1-chloro-2,4-dinitrochlorobenzol, 200 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, carbon disulfide, and 500 cc. of water were reacted according to the general procedure for 48 hours. The final dark red solution was steam-distilled and the residue of the steam distillate acidified with dil. acetic acid.

The yellow-brown precipitate was filtered and dried; yield, 35 g.

Anal. (Crude product). Calcd. for $\text{C}_7\text{H}_6\text{N}_2\text{S}_2$: S, 35.2. Found: 38.9.

This crude product could not be crystallized from the common organic solvents. The product was extracted with alcohol leaving a considerable amount of residue. The alcohol solution was treated with bone black. On evaporation of the alcohol a yellow solid was obtained which was crystallized from aniline.

The yield of this material was very small. It proved to be 5-amido-2-mercaptobenzothiazole; m. p., 215° .

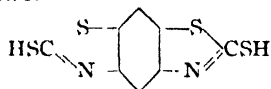
Anal. Calcd. for $\text{C}_7\text{H}_6\text{N}_2\text{S}_2$: S, 35.2; N, 15.35. Found: S, 35.40; N, 15.45.

If the crude product was not extracted with alcohol but was dissolved in hot pyridine and left standing for 24 hours, colorless rosetts had separated out. They were filtered and washed first with pyridine and then with ether.

For further purification this compound was once more crystallized from pyridine, as it proved to be insoluble in other solvents tried. It did not melt up to 270° .

Anal. Found: S, 50.60; N, 10.47.

This analysis checks for the following formula: dimercaptobenzodithiazole. Calcd. for $\text{C}_8\text{H}_4\text{N}_2\text{S}_4$: S, 50.00; N, 10.93.



The formation of this compound by the interaction of 2,4-dinitrochlorobenzol, sodium hydrosulfide and carbon disulfide is explained by assuming that the sulfur, formed by the violent reduction of the nitro groups, is introduced in *ortho* position to the nitro group in Position 4. This assumption is justified as it is known that sulfur reacts with certain organic amines to form aryl disulfides.⁹

Since it has already been shown that 5-amido-2-mercaptobenzothiazole cannot be formed by treating 2,4-dinitrochlorobenzol with sodium hydrosulfide and carbon disulfide, an attempt was made to prepare 2,4-diamidothiophenol as an intermediate product.

2,2',4,4'-Tetranitrodiphenyl Disulfide.—One hundred g. of 2,4-dinitro-1-chlorobenzol was dissolved in 1 liter of alcohol and a melt of 65.5 g. of $\text{Na}_2\text{S} \cdot 8\text{H}_2\text{O}$, and 9 g. of sulfur was added in small portions. A violent reaction took place and the 2,4,2',4'-tetranitrodiphenyl disulfide separated. To complete the reaction the mixture was heated under reflux on a sand-bath for three hours.

After cooling, the solution was filtered and the residue washed first with alcohol, then with warm water until free from sodium chloride; yield, 86 g. This compound decomposes at 280° , in agreement with Willgerodt.¹⁰

⁹ Schultz and Beyschlag, *Ber.*, 42, 743 (1909).

¹⁰ Willgerodt, *Ber.*, 17R, 352 (1884).

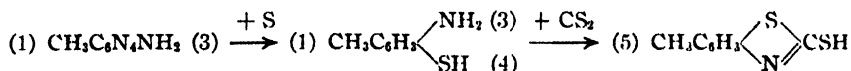
Reduction of 2,4,2',4'-Tetranitrodiphenyl Disulfide and Formation of 5-Amido-2-mercaptobenzothiazole.—Eighty-six g. of 2,4,2',4'-tetranitrodiphenyl disulfide is mixed with 350 g. of tin, and a mixture of 750 cc. of concd. hydrochloric acid and 750 cc. of water added. The solution is slowly heated on a sand-bath until the reaction is completed. Finally the solution is heated for two more hours to complete the reduction. The solution obtained is diluted with its own volume of hot water and filtered. The filtrate is evaporated to a small volume until crystals separate out and most of the excess of hydrochloric acid is evaporated. It is then diluted with seven times its volume of hot water and the solution de-tinned with hydrogen sulfide. The de-tinned solution is evaporated to a smaller volume and neutralized with sodium hydroxide; 150 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ is then added to the cold solution and hydrogen sulfide, previously saturated with carbon disulfide, is bubbled through until saturated. The solution is then heated on a sand-bath under reflux for 20 hours, while hydrogen sulfide, previously saturated with carbon disulfide, is bubbled through.

The solution is acidified with dil. acetic acid and the precipitate filtered off and washed with water. The residue is extracted with warm, aqueous ammonia and re-precipitated with dil. acetic acid.

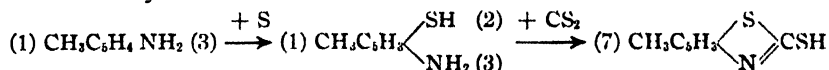
The precipitate is filtered, washed, dried and finally crystallized from freshly distilled aniline; yield, 38 g. of colorless needles; m. p., 216° .

Anal. Calcd. for $\text{C}_7\text{H}_7\text{N}_2\text{S}_2$: S, 35.2; N, 15.35. Found: S, 35.00; N, 14.97.

7-Methyl-2-mercaptobenzothiazole.—Sebrell and Boord² described the preparation of 3-monomethyl derivatives of 2-mercaptobenzothiazole, respectively, 4-, 5- and 6-methyl-2-mercaptobenzothiazole from the corresponding toluidines. They assume that 5-methyl-2-mercaptobenzothiazole is formed according to the following reaction scheme.



Theoretically, it would be possible for the following reaction to take place simultaneously.



In this case, the compound assigned as 5-methyl-2-mercaptobenzothiazole would be a mixture of 5- and 7-methyl-2-mercaptobenzothiazole.

To investigate this, an attempt was made to prepare 7-methyl-2-mercaptobenzothiazole. This is possible according to the new method of preparing substituted 2-mercaptobenzothiazoles from the corresponding *o*-nitrochlorobenzol compounds.

Commercial *o*-toluidine was purified by distillation and the mixed oxalates were prepared from the distillate separated according to the method of Holleman.¹¹

The preparation of 2-chloro-3-nitrotoluene from acetyl-*o*-toluidine is described by Cohen and Dakin.¹² An improvement of the latter part of the reaction is given by Holleman.¹¹

¹¹ Holleman, *Rec. trav. chim.*, **27**, 458 (1908).

¹² Cohen and Dakin, *J. Chem. Soc.*, **79**, 1127 (1901).

Reaction of 2-Chloro-3-nitrotoluene with Sodium Hydrosulfide and Carbon Disulfide.—Seven g. of 2-chloro-3-nitrotoluene, 30 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, and carbon disulfide were reacted according to the general procedure for four hours.

The final light red colored solution was steam-distilled, whereby some oil distilled (2-chloro-3-aminotoluene) and the residue acidified with dil. acetic acid.

The precipitate was filtered, washed with water and treated with warm aqueous ammonia. The sulfur was filtered off and the filtrate acidified with dil. acetic acid. The precipitate of 7-methyl-mercaptobenzothiazole was filtered, washed and dried; m. p. (dry), 176–180°. It was crystallized from aniline and then melted at 184°; yield, 2 g.

Anal. Calcd. for $\text{C}_8\text{H}_7\text{NS}_2$: S, 35.36; N, 7.73. Found: S, 35.75; N, 7.47.

As a by-product in this reaction 2-chloro-3-aminotoluene is formed, analogous to the formation of *o*-chloro-aniline from *o*-nitrochlorobenzol.

5-Methyl-2-mercaptobenzothiazole.—This compound could be prepared from 3-nitro-*p*-chlorotoluene, using *p*-toluidine as the starting material.¹³

Reaction of 3-Nitro-4-chlorotoluene with Sodium Hydrosulfide and Carbon Disulfide.—Five and one-half g. of 3-nitro 4-chlorotoluene, 20 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, hydrogen sulfide and carbon disulfide were reacted according to the general scheme. The next procedure was identical with the one described for 7-methyl-2-mercaptobenzothiazole; yield of dried, crude material, 3.2 g. It was crystallized from toluene, giving colorless needles; m. p., 171–173°.

This melting point is higher than indicated by Sebrell and Boord for the same compound prepared from *m*-toluidine. The assumption that their compound was a mixture of 5- and 7-methyl-2-mercaptobenzothiazole seems, therefore, to be justified.

Anal. Calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{S}_2$: S, 35.36; N, 7.73. Found: S, 35.85; N, 7.42.

2-Mercaptobenzothiazole-5-carboxylic Acid.—2-Nitro-4-cyano-1-chlorobenzol was prepared from *p*-chloro-aniline according to Mattaar.¹⁴

The saponification of 2-nitro-4-cyano-1-chlorobenzol was accomplished by dil sulfuric acid (1:1).¹⁵ The yield of 4-chloro-3-nitrobenzoic acid is almost quantitative. 4-Chloro-3-nitrobenzoic acid was treated with sodium hydrosulfide and carbon disulfide according to the general procedure described for previous *o*-chloronitrobenzol compounds.

Ten g. of 4-chloro-3-nitrobenzoic acid, 50 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, hydrogen sulfide and carbon disulfide reacted for six hours gave 6 g. of 2-mercaptobenzothiazole-5-carboxylic acid.

After cooling, the solution was acidified with dil. acetic acid and the precipitate filtered, washed and while still wet digested with warm aqueous ammonia. The solution was filtered from undissolved sulfur and the filtrate acidified with dil. acetic acid. The precipitate was filtered and dried; yield, 6 g.

This compound was difficultly soluble in water and cold alcohol and slightly soluble in warm glacial acetic acid.

It was crystallized from glacial acetic acid, giving white needles which did not melt up to 270°.

Anal. Calcd. for $\text{C}_8\text{H}_5\text{O}_2\text{NS}_2$: S, 30.33; N, 6.63. Found: S, 29.88; N, 7.01.

To prove the presence of a carboxyl group this compound was titrated in 50% alcohol-water solution, with 0.1 *N* sodium hydroxide solution, using phenolphthalein as an indicator.

Titration. Calcd. for $\text{C}_8\text{H}_5\text{O}_2\text{NS}_2$: 28.43 cc. Found: 28.40 cc.

¹³ Gattermann, *Ber.*, 18, 2600 (1885).

¹⁴ Mattaar, *Rec. trav. chim.*, 41, 24 (1922).

¹⁵ Claus and Kurz, *J. prakt. Chem.*, [2] 37, 200 (1888).

Attempts to Prepare Dichloro-2-mercaptobenzothiazole.—Attempts were made to prepare dichloro-substituted 2-mercaptobenzothiazoles by the general procedure described above from (1) 1,2,4-trichloro-*o*-nitrobenzol, prepared as described by Lesimple;¹⁶ (2) 2,2'-dinitro-4,5,4',5'-tetrachlorodiphenyl disulfide, obtained from *o*-dichlorobenzol as described by Blanksma.¹⁷

In both cases compounds were obtained which indicated that one chlorine atom was replaced by a mercaptan group. However, the yields of the products were very poor and no effort has been made to clear up their exact structure.

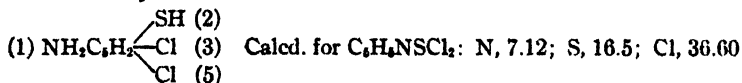
(3) *p*-NITRO-ANILINE.—It was thought that a dichloro-2-mercaptobenzothiazole could be formed from 2,2',4,4'-tetrachloro-6,6'-dinitrodiphenyl disulfide, which is obtained from *p*-nitro-aniline as described by Holleman and Blanksma.¹⁸

Seventy g. of this material, m. p., 190°, and 200 g. of Na₂S·9H₂O dissolved in 500 cc. of water and treated according to the general procedure gave 22 g. of a colorless, amorphous powder.

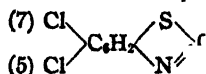
This material was crystallized from xylene and gave 18.5 g. of colorless needles; m. p., 213°.

Anal. Found: N, 7.12; S, 15.10; Cl, 36.52.

The analysis checks for the formula



and not for the expected compound



We have here a remarkable case where the ring closing of the *o*-amidothiophenol to the thiazole ring is prevented by the other substituents present. Under what conditions the ring closing can occur will be investigated later. As a substituted thiophenol this compound is new in its class.

Summary

A new method for the preparation of 2-mercaptobenzothiazole is described, which is especially suitable for laboratory use. This method was extended to several new derivatives and is especially suitable for the monohalogen derivatives. The general synthesis could not be applied for the dihalogenated 2-mercaptobenzothiazoles.

AKRON, OHIO

¹⁶ Lesimple, *Ann.*, 137, 123 (1866).

¹⁷ Blanksma, *Rec. trav. chim.*, 21, 419 (1902).

¹⁸ Holleman and Blanksma, *ibid.*, 23, 366 (1904); 27, 48 (1908).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
SASKATCHEWAN]

ACTION OF BENZYLAMINE ON GLUCOSE IN ACETIC ACID SOLUTION. III

By C. N. CAMERON

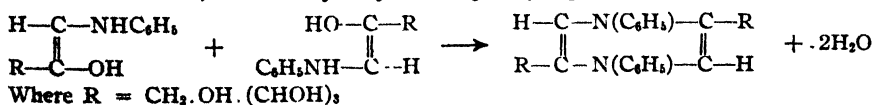
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The reaction between amines and glucose is being studied in the hope that it may throw some light on the reaction of amino acids and carbohydrates. Not only do aromatic and aliphatic amines react with carbohydrates, but amino acids do also, and apparently in a similar manner. Thus Irvine and his collaborators have shown that alanine¹ and *o*-aminobenzoic acid² react with glucose in the cold just as aniline does. However, when *o*-aminobenzoic acid is heated with glucose, extensive decomposition occurs and little of the *o*-carboxy-anilide can be isolated. Similarly, it has been shown that when glucose and glycine³ are heated in water solution, cyclic condensation products containing nitrogen are formed. Again, it is found that there is the greatest increase of "humins" nitrogen from dextrose and protein hydrolysates⁴ when the solution is neutral or weakly acid. This shows that glucose may react directly with the amino acids and that this compound may give rise to the humins.

When glucose is allowed to react with amines such as aniline⁵ in the presence of acetic acid, apparently the same type of reaction occurs. First a compound, glucose-anilide, is formed and this in the presence of acid undergoes further changes; glucose-anilide disappears and brown condensation products are formed.

The latter change is still the subject of study, but tentatively the following explanation is offered. It has already been indicated that glucose-anilide in acid solution becomes "reactive." This might be due to the formation of the aldehyde isomer, which then may change to the enol or break down to methyl glyoxal. If the enol does form, then there may be formed nitrogen ring compounds of various types of which the formation of 2,5-ditetroxybutyl-1,4-diphenyl pyrazine is an example.



This would be similar to the formation of 2,5-ditetroxybutyl pyrazine⁶ from fructose and ammonia in methyl alcohol solution.

¹ Irvine and Hynd, *J. Chem. Soc.*, 99, 161 (1911).

² Irvine and Gilmour, *ibid.*, 95, 1545 (1909).

³ Maillard, *Compt. rend.*, 154, 66 (1912).

⁴ Dowell and Menaull, *J. Biol. Chem.*, 40, 131 (1919).

⁵ Cameron, *THIS JOURNAL*, 48, 2233, 2737 (1926).

⁶ Stolte, *C. A.*, 2, 1978 (1908).

On the other hand, it was noticed that glucose-benzylamide residues in methyl alcohol containing acetic acid which had been left exposed to the air became colored, and a distinctly quinoline-like odor developed. Hence it was thought that methyl glyoxal or pyruvic acid might be formed from the "reactive" glucose and that one of these and the amine gave rise to the colored product. This would be comparable to the formation of pyrazine derivatives from ammonia and phenyl glyoxal,⁷ or to the production of methyl cinchoninic acid from aniline and pyruvic acid.⁸

It has been found, in fact, that alcoholic solutions of glucose-benzylamide containing acetic acid, in 24 hours gave a test for methyl glyoxal;⁹ also, that solutions of benzylamine, glucose and acetic acid in alcohol soon give the same test, the time varying with the concentration of the reactants. Solutions of benzylamine and glucose did not give the test during the time of observation. As a test which depends upon a change of color of sodium nitroprusside in alkali and in acid is liable to be misleading, an attempt was made to isolate the methyl glyoxal as the osazone. It was found that by adding *p*-nitrophenylhydrazine to solutions of glucose, benzylamine and acetic acid, the corresponding osazone of methyl glyoxal¹⁰ slowly forms and can be identified. Similarly, from acid solutions of glucose-benzylamide in the presence of *p*-nitrophenylhydrazine, the same osazone is formed in small amounts. Apparently, then, one of the products of the action of benzylamine and glucose in the presence of acetic acid is methyl glyoxal and this, of course, may react with the benzylamine to give various nitrogen ring compounds, but whether this is the only mechanism is still an open question.

Experimental Part

Preparation of Glucose-benzylamide.—Ten g. of glucose was dissolved in 200 cc. of hot 95% alcohol and 17.8 g. (3 molecular proportions) of benzylamine added. The reaction mixture was heated for ten minutes at boiling; it was filtered hot and allowed to stand for 48 hours. It was then cooled in ice water and a gelatinous precipitate separated. This was removed by filtration, thoroughly washed with anhydrous ether and dried in a vacuum. This method yielded a slightly yellow substance, m. p. 70–75°, the yields varying from 80–85%. A 3% solution in methyl alcohol gave $\alpha = -0.61$ to -0.52° in 24 hours in a 1-dcm. tube.

Glucose-benzylamide, recrystallized four times from methyl alcohol and anhydrous ether, is a colorless substance with a bitter taste. It is somewhat soluble in water, but solution is slow. Rather easily hydrolyzed, it reduces Fehling's solution on heating. It is quite soluble in cold methyl and in hot ethyl alcohol, but from the latter it separates as a gel on cooling; it is only slightly soluble in ligroin, benzene, ether and ethyl acetate. The pure material melted at 81.5°; a 3% solution in methyl alcohol gave $\alpha = -1.28$ to -0.68° in 24 hours in a 1-dcm. tube, whence $[\alpha]_D^{25} = -22.66^\circ$.

⁷ Pinner, *Ber.*, **38**, 1531 (1905). See also Gastaldi, *C. A.* **16**, 112 (1922).

⁸ Simon, *Ann. chim. phys.*, [7] **19**, 433 (1896).

⁹ Neuberg, *Biochem. Z.*, **71**, 150 (1915).

¹⁰ Dakin and Dudley, *J. Biol. Chem.*, **15**, 130 (1913).

Anal. Calcd. for $C_{12}H_{15}O_5N$: C, 57.96; H, 7.12; N, 5.20. Found: C, 57.92; H, 7.19; N, 5.24.

Glucose, Benzylamine and Acetic Acid.—When glucose is allowed to react with benzylamine in ethyl alcohol at room temperature and the reaction is followed by means of the polariscope, it is found (Table I) that during the first six hours the rotation becomes very slightly more positive, then gradually less positive and finally negative. That is, the reaction is of the same type as those previously studied by Irvine.¹¹ When acetic acid is also present, the preliminary lag in the rotation is not apparent; the rotation gradually became negative just as was the case with aniline, glucose and acetic acid.

TABLE I

EFFECT OF ACETIC ACID ON THE REACTION BETWEEN GLUCOSE AND BENZYLAMINE
Glucose, 1.5 g.; ethyl alcohol to 50 cc.; tube, 1 dcm.; temp., 22–24°.

Benzylamine acetic acid Time	3 mole propn. None α	3 mole propn. α	6 mole propn. None	6 mole propn. α
5 min.	+1.72	+1.28	+1.74	+0.30
1 hour	+1.72	+0.42	+1.73	— .04
6 hours	+1.76	+ .08 ^a	+1.79	— .27 ^a
1 day	+1.28	— .32	+1.26	— .92
3 days	—0.50	— .88	—0.52	Red
4 days	— .82	Red	— .89	
8 days	—1.16 ^a		—1.18 ^a	

^a First tinge of yellow noted.

Effect of Changing the Concentration of Acetic Acid on the Reaction between Glucose and Benzylamine.—As glucose solutions containing benzylamine and acetic acid in a 1:1 proportion were acid to litmus five minutes after mixing, it seemed worth while to study the reaction when the ratio of amine to acid was in other proportions, in an attempt to keep the reaction near the neutral point. The result is shown in Table II.

TABLE II

EFFECT OF CHANGE OF CONCENTRATION OF ACETIC ACID ON THE REACTION BETWEEN
BENZYLAMINE AND GLUCOSE

Glucose, 1.5 g.; benzylamine, 0.89 g. (mole propn.); alcohol to 50 cc.; tube, 1 dcm.; temp., 23–24°.

Acetic acid Time	None (1) α	0.5 mole propn (2) α	0.75 mole propn. (3)	1 mole propn. (4)
5 min.	+1.73	+1.70	+1.68	+1.66
15 min.	+1.74	+1.64	+1.53	+1.48
30 min.	+1.73	+1.53	+1.37	+1.28
1 hour	+1.73	+1.39	+1.06	+1.08
2 hours	+1.74	+0.96	+0.73	+0.93
3 hours	+1.76	+ .63	+ .62	+ .88
6 hours	+1.76	+ .27	+ .57	+ .80
1 day	+1.45	+ .12	+ .33	+ .52
4 days	—0.08	— .27	— .28	— .22
5 days	— .07	Yellow	Orange	Orange-red

¹¹ (a) Irvine and Gilmour, *J. Chem. Soc.*, 93, 1429 (1908). (b) Irvine and Nicoll, *ibid.*, 97, 1449 (1910).

The hydrogen-ion concentration was followed approximately by means of indicators. Reaction mixture No. 1 was alkaline to phenolphthalein during 20 days. No. 2 was alkaline on mixing, but gradually the alkalinity diminished until in six hours phenolphthalein was not affected and in two days it became slightly acid to litmus and remained thus for 20 days. On mixing, No. 3 was slightly alkaline, but in 30 minutes it had no effect on phenolphthalein; in three hours it was slightly acid to litmus and remained acid. The fourth solution became faintly acid to litmus 15 minutes after mixing and remained acid thereafter.

It might be pointed out, then, that Reaction 2 (Table II) took place, colored material was produced, it gave the test for methyl glyoxal described later and yet the hydrogen-ion concentration at all times was not far from the neutral point. Curiously also this reaction, slower at first, was most rapid as measured by the change in rotation during a 24-hour period.

Glucose-benzylamide and Acetic Acid.—The colored material produced in glucose, benzylamine and acetic acid solutions is due first (a) to the formation of glucose-benzylamide and then (b) to the action of acetic acid on this compound as indicated by the following.

(a) To an alcohol solution of 3 g. of glucose were added 5.35 g. of benzylamine and 3 g. of acetic acid and the solution was made up to 50 cc. After three days, a large excess of anhydrous ether was added to the ice-cooled reaction mixture and the gelatinous precipitate which separated was removed by filtration. This material was glucose-benzylamide; yield, 0.55 g.; m. p., 80–81°; 0.3422 g. in 25 cc. of methyl alcohol gave $\alpha = -0.30^\circ$ in a 1-dcm. tube, hence $[\alpha]_D^{25} = -21.9^\circ$.

(b) It was found that a 3% solution of glucose-benzylamide in methyl alcohol, in a 1-dcm. tube, gave $\alpha = -1.27^\circ$ in five minutes, -0.69° in 24 hours and -0.64° in 24 days. The solution was colored only a light yellow in 40 days. A comparable solution, containing 0.67 g. of acetic acid in 100 cc. of a 3% solution of glucose-benzylamide in methyl alcohol gave, in a 1-dcm. tube, $\alpha = -0.69^\circ$ in five minutes and -0.42° in six hours. It became light yellow in one day and was red-brown in seven days.

Test for Methyl Glyoxal.—It was found that alcohol solutions of glucose-benzylamide, containing acetic acid and solutions of glucose, benzylamine and acetic acid gave the following test for methyl glyoxal, whereas comparable blanks did not.

To 0.5 cc. of the solution, suspected to contain methyl glyoxal, was added 0.5 cc. of freshly prepared solution of 2% sodium nitroprusside. On the addition of 0.5 cc. of 10% sodium hydroxide the mixture turns red if methyl glyoxal is present. When the reaction mixture is made acid with acetic acid, a violet color is produced. This color, as a rule, persists for some time.

When the test was applied to 3% alcohol solutions of glucose, fructose, glucose-benzylamide, glucose and benzylamine (1, 3 and 6 molecular proportions) during a period of 24 days, the alkaline mixture was yellow; on acidifying with acetic acid, an amber color developed. On the other hand, a 3% solution of glucose-benzylamide in alcohol, containing 0.67 g. of acetic acid (1 molecular proportion) gave a slight test in six hours, a positive test in one day and continued to give it for at least 30 days.

Similarly, alcohol solutions of glucose (3%), benzylamine and acetic acid (1, 3 and 6 molecular proportions, as in Table I) gave a positive test for methyl glyoxal in one day after mixing, and continued positive.

***p*-Nitrophenylosazone of Methyl Glyoxal.**—To 100 cc. of a 48-hour old solution of 3% glucose containing benzylamine and acetic acid (3 molecular proportions), were added 1 g. of *p*-nitrophenylhydrazine and 0.35 cc. of glacial acetic acid. The reaction mixture was shaken until the phenylhydrazine had dissolved and was then filtered from a slight residue. An amorphous precipitate slowly formed and in six days this was removed. The amount was so small that nothing definite could be decided. A further 1 g. of *p*-nitrophenylhydrazine was added, and 40 days after the first addition of phenylhydrazine the precipitate was removed. The precipitate was washed with hot alcohol and dried in a vacuum. It weighed 0.18 g.; m. p., 260–269°, with decomposition. It gave the test for the *p*-nitrophenylosazone of methyl glyoxal.¹⁰ The precipitate was washed with hot 10% sodium carbonate solution, then with water, alcohol and ether. The alkaline filtrate gave no precipitate on acidifying with acetic acid, showing the absence of the *p*-nitrophenylhydrazone of pyruvic acid. The original precipitate was recrystallized from nitrobenzene and toluene; the crimson needles obtained weighed 0.10 g.; m. p., 299–300°. When mixed with the *p*-nitrophenylosazone of methyl glyoxal, the melting point was unchanged. Other samples of a similar material were obtained and analyzed.

Anal. Calcd. for $C_{15}H_{14}N_4O_4$: N, 24.56. Found: 24.62.

In acid solutions of glucose-benzylamide containing *p*-nitrophenylhydrazine, the amorphous precipitate forms only very slowly. Thus in 40 days only 0.08 g. of material was obtained from 100 cc. of a methyl alcohol solution of 3 g. of glucose-benzylamide, 2 g. of *p*-nitrophenylhydrazine and 1.8 g. of acetic acid. This precipitate, when purified, melted at 297–298° and gave the color test for the *p*-nitrophenylosazone of methyl glyoxal.

Glucose-Benzylamide in Water.—It has been found that with glucose, aniline and acetic acid or with glucose-anilide and acetic acid in water solution, a brown precipitate gradually forms and it was thought that glucose-benzylamide would react in a similar manner. Apparently, however, this substance in water hydrolyzes directly to glucose and benzylamine (Table III); the solutions do not yield colored products nor do they give the test for methyl glyoxal.

TABLE III
GLUCOSE-BENZYLAMIDE IN WATER

Glucose-benzylamide, 0.5 g.; water to 50 cc.; tube, 1 dcm.; temp., 20–22°.

Acetic acid Time ^a	None α	0.11 g. (1 mole propn.) α
5 min.	–0.43	+0.10
15 min.	–.42	+ .31
30 min.	–.42	+ .33
1 hour	–.40	+ .34
1 day	–.80	+ .34
2 days	–.23	+ .35
24 days	+ .14	

^a Time was computed from contact of the glucose-benzylamide and water, but with acid present from the time of addition of the acid, five minutes after solution.

Glucose-benzylamide in water slowly hydrolyzed until in 36 days the solution became opalescent due to the separation of benzylamine. During 80 days, no coloration was noted and no test for methyl glyoxal was obtained. With 1 molecular proportion of acetic acid present the glucose-benzylamide quickly hydrolyzed, so that in 30 minutes it was practically complete. (Complete hydrolysis of 0.5 g. of glucose-benzylamide should give a rotation of $+0.35^\circ$.) In 80 days, no color developed and the methyl glyoxal test was negative. Even with a small concentration of acid present, as in the experiment below, in 80 days there was no colored precipitate and no test for methyl glyoxal but the reaction mixture had a slight quinoline-like odor.

To 0.5 g. of glucose-benzylamide in water, 0.028 g. of acetic acid (0.25 molecular proportion) was added and the solution made up to 50 cc. Five minutes after the addition of acid and 15 minutes after contact of the amide and water, the rotation in a 1-dcm. tube was -0.28° , in six days it was -0.08° and in 24 days, -0.20° .

Glucose, Benzylamine and Acetic Acid in Water.—The following experiments indicate that benzylamine and glucose in water react to form glucose-benzylamide. However, with 1 molecular proportion of acetic acid present, no reaction apparently occurs, which would be expected from the action of acid on glucose-benzylamide in water. Apparently acetic acid catalyzes the hydrolysis of glucose-benzylamide to a greater extent than it does the "activation." Then one would expect that with a low concentration of acid, activation might occur and brown products form. This is found to be true.

To a water solution of 1.5 g. of glucose was added 0.89 g. of benzylamine (1 molecular proportion) and 0.5 g. of acetic acid (1 molecular proportion) and the solution was made up to 50 cc. During six days (at $20-21^\circ$) there was no change in rotation and the test for methyl glyoxal was negative. In 80 days, no colored material had formed.

To a water solution of 1.5 g. of glucose was added 0.45 g. of benzylamine (0.5 molecular proportion) and the solution was made up to 50 cc. In six days (at $20-21^\circ$) the rotation in a 1-dcm. tube had changed from -1.51 to -0.40° , but thereafter the reaction mixture became opalescent due to the separation of a small amount of glucose-benzylamide. During 20 days it gave no test for methyl glyoxal and in 80 days no colored precipitate.

A similar glucose solution, containing 0.89 g. of benzylamine (1 molecular proportion) and 0.06 g. of acetic acid (0.0125 molecular proportion) in 50 cc., was cloudy from the start and the rotation could not be read. During 20 days the test for methyl glyoxal was negative but gradually a small amount of brown oil collected and the solution had a nicotine-like odor. After 80 days (at $20-21^\circ$) the oil was extracted with ether, the ether evaporated and the residual oil fused with potassium hydroxide, when a quinoline-like odor was detected. However, the amount of material was too small to ensure any definite conclusions as to its nature.

Summary

It is shown that in alcohol, benzylamine and glucose in the presence of acetic acid react to form glucose-benzylamide and that the latter is then, in part at least, converted into methyl glyoxal. The methyl glyoxal, presumably, reacts with the amine to form nitrogen ring compounds. It is found that the acetic acid catalyzes the reaction between benzylamine and glucose and that even small amounts of acid are effective,

so that the production of the methyl glyoxal may occur in reaction mixtures which are near the neutral point.

In water solutions, glucose does not react with benzylamine in the presence of acetic acid, when the amine and acid are in a one to one ratio but when the amount of acid used is very small, then reaction does occur as in alcohol. Glucose-benzylamide in water solution is hydrolyzed very readily to the constituent compounds, and the formation of methyl glyoxal or nitrogen ring compounds was not apparent under these conditions.

SASKATOON, SASKATCHEWAN, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MECHANISM OF THE CHANGE OF ISONITRO TO NITRO COMPOUNDS

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Introduction

It has been shown by Hantzsch¹ that the reversible electrolytic dissociations of nitromethanes are slow enough in both directions to permit the measurement of the rates of change of electrical conductivity when nitromethanes react with bases to form salts or when nitromethanes are formed from their salts by reaction with hydrogen ion. He explained the anomalously slow rates of these homogeneous ionic reactions as due to accompanying changes of structure. The formula RCH_2NO_2 has been accepted as that of the nitromethanes, while the alternative formulas $\text{RCH}=\text{N}\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O}^- \end{smallmatrix}$ and $\text{RCH}-\text{N}-\text{O}^-$ have been assigned to the ions. Hantzsch prefers

the latter formula. This theory is supported by the existence of an isomeric but unstable form of phenylnitromethane, which can be obtained from solutions of the salts of phenylnitromethane by rapid precipitation with hydrochloric acid.

Hantzsch's measurements of the rates of these reactions are not sufficiently accurate to show the mechanisms of the changes, although they do indicate that these are somewhat complex. We have, therefore, attempted to elucidate the mechanisms of these reactions through more accurate measurements of the rates.

Phenylnitromethane and nitromethane were chosen as examples of aryl-substituted and purely aliphatic nitromethanes, respectively, both of these substances having previously been used by Hantzsch. *p*-Nitrophenol was chosen as an example of a different type of nitro compound

¹ Hantzsch, *Ber.*, 29, 2251 (1896); 32, 607 (1899).

whose behavior as an acid is presumably also accompanied by a change in structure.

The rates were measured only for the reactions in one direction, that of the formation of the nitro compounds by the combination of the ions. They were carried out at two temperatures in each case, in order to see whether the heats of activation for the reactions were markedly different for these types of nitro compounds.

The conditions under which the experiments were carried out, that is, at low temperatures, in dilute solutions, and without excess of acid, were such that secondary decompositions of the nitro compounds, even of nitromethane, were negligible.

Experimental Part

General Method.-- Solutions containing equivalent amounts of the sodium salt of the nitro compound in question and of hydrochloric acid were mixed. The normality of each solution was 0.01 and equal volumes of the solutions were used, so that after mixing, the resulting solution was 0.005 *N* with respect to both sodium chloride and the isonitro acid. The solvent for all the solutions was a mixture of methyl alcohol and water, containing 500 cc. of the former substance per liter of the solution. These concentrations are such that no substance crystallizes out during the experiment, even at -24° . The same solvent was used to make up both solutions so as to avoid the heating effects due to mixing methyl alcohol and water. The solutions were cooled to the temperature of the thermostat, and then thoroughly mixed. This process was carried out with the minimum removal of the flasks from the thermostat. Blank experiments showed that this could be done without raising the temperature of the solutions more than 0.1° . When mixed, the solution was rapidly sucked into a conductivity cell, which had also been allowed to reach the temperature of the bath. This cell was essentially a U-shaped tube with two bulbs, into one of which platinum plate electrodes were sealed and afterwards platinized. The ends of the tubes were supplied with stopcocks, so that when these were shut no changes of the level of the liquid could occur during the experiment.

Measurements of the conductivity were then made at different times, over a range corresponding to a 100-fold change of concentration of the pseudo nitro compound. The final conductivity was obtained by allowing the solution to stand until all significant changes of conductivity had taken place, and then measuring the conductivity. This measurement was preferred to that obtained by measuring the conductivity of 0.005 *N* sodium chloride solution, as it avoids the errors and delay which occur when a level has to be adjusted to a mark. Further, the use of the final conductivity instead of that of a 0.005 *N* solution of sodium chloride

automatically corrects for any reversibility of the reactions in cases, such as these, in which the reactions are very nearly completed. However, the differences between the final conductivities and that of 0.005 *N* sodium chloride are not greater than those which could be produced by filling the tubes to different levels.

Source of Chemicals.—The phenylnitromethane was prepared by the action of benzyl bromide on silver nitrite. It was purified by precipitating its sodium salt from an ethereal solution of the phenylnitromethane with a solution of sodium methylate in methyl alcohol. The salt was then taken up in water, and the aqueous solution was freed from practically neutral substances, for example, benzyl alcohol, by washing it with ether. The phenylnitromethane was precipitated from the aqueous solution of its salt with carbon dioxide. It was then fractionally distilled in a vacuum.²

The nitromethane, a Kahlbaum preparation, was purified by fractional distillation. A fraction which distilled between 100.5 and 101.5° was used.

The *p*-nitrophenol was also a Kahlbaum preparation. It was purified by crystallization from water; *m. p.*, 114°.

The standard solutions of the salts of the nitro compounds were prepared by dissolving weighed quantities of the nitro compounds in 0.01 *N* solutions of sodium hydroxide. The sodium hydroxide was standardized against the hydrochloric acid solutions, using phenolphthalein as the indicator. The sodium hydroxide used contained traces of carbonate, but this was an advantage, as the presence of the carbonate prevents any appreciable excess of either hydrogen ion or of the negative ion of the isonitro compound, which might be produced by a failure to measure out or mix exactly equivalent amounts of the acid and alkali.

Measurement of the Conductivities.—The usual conductivity set was used. It consisted of an Edison potassium hydroxide battery giving 6.7 v., 1000-cycle Leeds and Northrup oscillator, a standard four-dial resistance box with a maximum resistance of 9999 ohms, a Kohlrausch slide-wire bridge of Leeds and Northrup make and a set of Murdock headphones.

Preliminary runs were always made, during which the cell was balanced for capacity, so that during the experiments sharp minima could be obtained without delay.

The conductivities were measured with an accuracy of about 0.1%. However, as the conductivities are only partly due to the conductivities of the isonitro acids the actual accuracy of any measurement is much less, more especially near the end of a run.

Temperature Control.—A gallon (3.8-liter) Dewar flask was used as a thermostat. The bath liquid in every case was in equilibrium with a solid phase, and was stirred mechanically throughout the runs, except during the times when the minima of sound in the phones was being observed. The constant-temperature systems used were carbon tetrachloride in equilibrium with solid carbon tetrachloride, water in equilibrium with ice, benzene in equilibrium with solid benzene, and a mixture

² We thank Messrs. M. A. Joslyn and C. Judah, students at this university, for this preparation of our phenylnitromethane.

of methyl alcohol and water, 1 to 10 by volume, in equilibrium with ice. Although this last is a two-component system, it gave a temperature as constant as the other systems, due to the fact that the heat flow through the Dewar flask during the experiment was equivalent to the heat of solution of an amount of ice quite negligible with respect to the water present in the liquid phase. The temperatures were measured from time to time during the runs, and at different parts of the bath. During none of the runs reported in this article was any variation of temperature greater than 0.05° with respect to both time and place observed.

Owing to the great dilution of the reagents, the heat of the reaction is quite small with respect to the heat capacity of the reacting solutions, so that no rise in temperature greater than 0.1° could have taken place through the mixing of the reagents. The heat of mixing methyl alcohol and water was avoided by making up the solutions with the already mixed solvents.

Experimental Results

The results obtained are shown graphically in eight curves. In these curves the common logarithms of the conductivities due to the isonitro acids are plotted against the times which have elapsed after mixing. In each case the conductivity of the final solution is taken as the unit of conductivity. In every case except Curve 8 the final solution was a $0.005\ N$ solution of sodium chloride. In Curve 8 a slight excess of hydrochloric acid was present. The conductivity of the isonitro acid, expressed in terms of the final solution, was obtained by subtracting the final conductivity from the measured conductivity and dividing the result by the final conductivity. Throughout this paper, this quantity is represented by the letter c .

The value of c is proportional to the concentration of the negative ion of the isonitro acid during any run, as the changes of mobility of the ions are negligible during an experiment (the solutions are very dilute) and the total conductivities never change more than 40% . The results of a typical experiment are shown in Table I.

TABLE I

RATE OF FORMATION OF *p*-NITROPHENOL FROM ITS IONS AT -23.6°

Initial concentrations: *p*-isonitrophenol, $0.005\ N$; sodium chloride, $0.005\ N$

Time, min.	Conductivity, mhos $\times 10^{-4}$	c	Time, min.	Conductivity, mhos $\times 10^{-4}$	c
2	2.350	0.2730	11	1.872	0.0141
3.25	2.140	.1593	14	1.857	.0060
6	1.976	.0704	17	1.850	.0022
8	1.914	.0368	22	1.846	.0000
9	1.891	.0243	Infinity	1.846	.0000

Curves 1, 2, 3, 4, 5 and 6 represent experiments in which the initial concentrations were $0.005\ N$ with respect to the isonitro acid and to

sodium chloride. Curves 1 and 2 represent experiments on phenylisonitromethane at 0 and 5.2°, respectively. Curves 3 and 4 represent experiments on isonitromethane at -23.8 and 0°, respectively. Curves

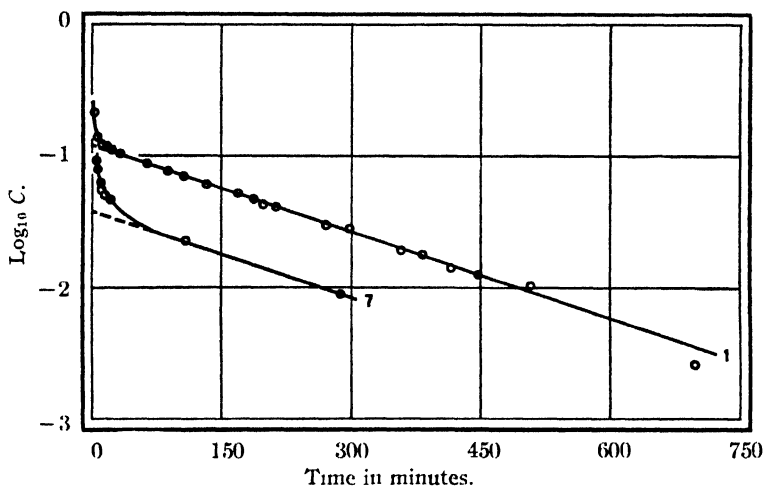


Fig. 1.—Change of conductivity during the formation of phenylnitromethane from its salt at 0°. Initial concentration, 1, 0.005 *N*; 7, 0.002 *N*.

5 and 6 represent experiments on *p*-isonitrophenol at -23.6 and -9.8°, respectively. Curve 7 represents an experiment on phenylisonitromethane at 0° in which the initial concentration of the isonitro acid was 0.002 *N*,

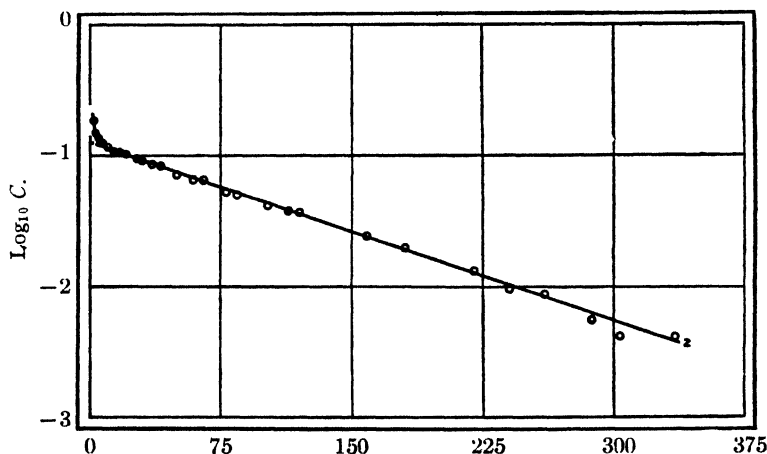


Fig. 2.—Change of conductivity during the formation of phenylnitromethane from its salt at 5.2°. Initial concn., 0.005 *N*.

while that of the sodium chloride was 0.005 *N*. Curve 8 represents an experiment in which about 10% excess of hydrochloric acid was present,

but which otherwise was identical with the experiment represented by Curve 4.

The curves are all twofold in character. They are concave upwards at the start, but become straight lines as the reactions proceed. The curved portions of the graphs must represent reversible formations of isonitro compounds by combinations of ions, and an accompanying change of structure, as the reactions are not instantaneous. These reactions

may be represented by the type equation, $\text{RCH}=\text{N} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O}^- + \text{H}^+ \rightarrow \text{RCH}-\text{N}-\text{OH}$. The linear portion of the graphs must represent isomeric changes of the ions, whose reversals are prevented by very rapid

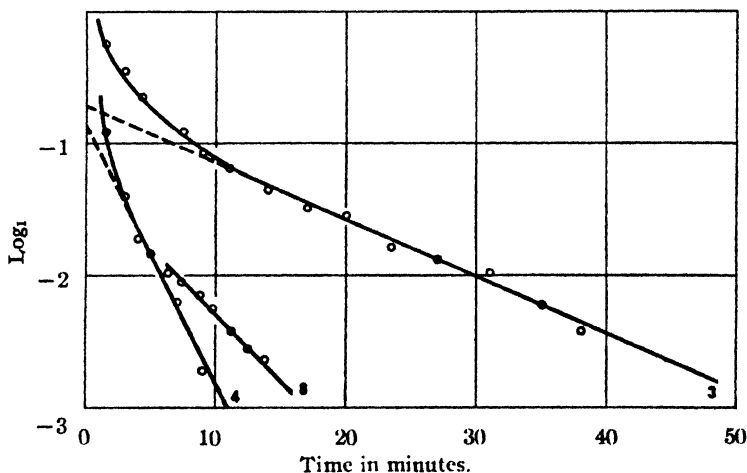


Fig. 3.—Change of conductivity during the formation of nitromethane from its salt: 3, initial concn., 0.005 *N*, *T*, -23.8° ; 4, initial concn., 0.005 *N*, *T*, 0° ; 8, initial concn., 0.005 *N*, *T*, 0° , HCl present.

combinations with hydrogen ion to form the true nitro compounds. These

changes may be represented by the type equations, $\text{RCH}=\text{N} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O}^- \rightarrow \text{RCHNO}_2$, and $\text{RCHNO}_2 + \text{H}^+ \rightarrow \text{RCH}_2\text{NO}_2$. The reasons why the experiments show these steps in the reactions are discussed in the following section.

Discussion of Results

If the isonitro acids are partially ionized and change irreversibly to the un-ionized nitro compounds, the courses of the reactions may be followed by conductivity measurements, but the rates of decrease of the

conductivities are not proportional to the rates of formation of the unionized compound, because the fraction of any reactant which is ionized increases as its concentration decreases. However, if we assume that the mobilities of the ions are constant during the reaction, that the activities are proportional to the concentrations and that the purely ionic reactions are rapid with respect to the reactions involving changes of structure,³ then we can obtain equations expressing the rate of change of conductivity as a function of the conductivity, in which the nature of the function depends on the mechanism of the reaction. Thus, if the rate-determining

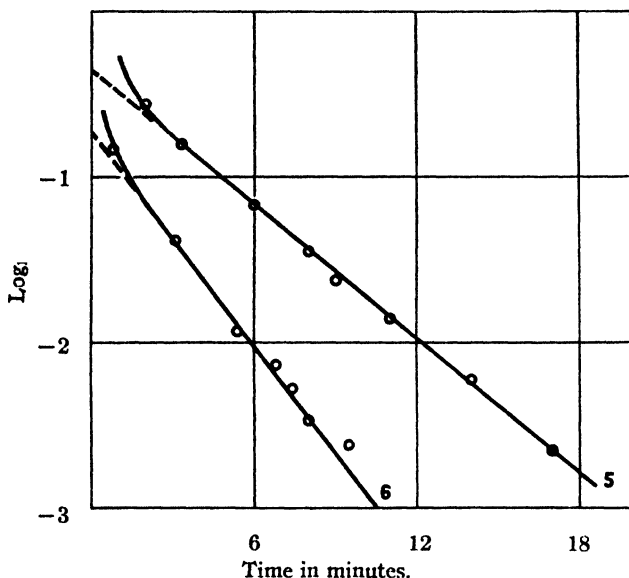


Fig. 4.—Change of conductivity during the formation of *p*-nitrophenol from its salt: 5, initial concn., 0.005*N*, *T*, −23.6°, 6, initial concn., 0.005*N*, *T*, −9.8°.

reaction is a monomolecular change of the ion of the isonitro acid to an ion which immediately combines with a hydrogen ion to form the nitro compound, the equation will be

$$-dc/dt = kc/[2c/(KR) + 1] \quad (1)$$

where *c* is the conductivity due to the isonitro acid, *k* is the rate of reaction constant, *K* is the dissociation constant of the isonitro acid, while *R* is a proportionality constant connecting the conductivity, *c*, with *i*, the concentration of the ion of the isonitro compound, by the equation

³ All of these assumptions are valid when the solution is very dilute and the change of conductivity during the reaction is small, and both of these conditions exist in our measurements.

$c = Ri$. On the other hand, if the master reaction is a monomolecular change of the undissociated isonitro acid to the nitro compound, then the equation connecting the rate of change of conductivity with the conductivity is

$$-dc/dt = k/KR \cdot [(2c/KR) + 1] \quad (2)$$

These equations would give different types of curves if $\log c$ were plotted against time. The curve corresponding to Equation 1 would be concave downwards at high values of c , but would become a straight line as c decreases. On the other hand, the curve which would be obtained from Equation 2 would be a straight line at the beginning, but would become concave upwards, eventually corresponding to the curve of a second-order reaction. Whether the plot of an actual series of measurements would show these peculiarities would depend on the range of values over which c was measured, and on the values of R and K .

The experimental curves (1, 2, 3, 4, 5, 6) belong to neither of these types. They are all concave upwards at the beginning and then become linear, these changes being too abrupt for the curves to represent a combination of Equations 1 and 2. Variations in temperature of sufficient magnitude to produce the effects observed were quite impossible. The only explanation of such curves is that there are two simultaneous reactions or mechanisms of reaction, one of which becomes subordinate to the other as the reaction proceeds. This disappearance of one of the reactions may be either due to its higher order, or because it reaches a steady state, and since, in every case, the two reactions differ markedly in rate, the steady states must be approximately equal to the true equilibria.

These two alternatives are very easily distinguished, for if equilibrium is reached only after a lapse of time, the slope of the curve depends not only on the conductivity, but also on the time, as long as this time is short. On the other hand if the disturbing reaction becomes insignificant because it is a high-order reaction, then the slope of the curve depends only on the conductivity.

To settle this point Expt. 7 was performed. In this experiment all of the conditions were identical with those of Expt. 1, except the initial concentrations of phenylisonitromethane. A comparison of the curves obtained from the two experiments (Fig. 1) shows that they are not superimposable at the beginning, but that after sufficient time has elapsed to allow the steady state to be established, the two curves become identical. This experiment shows conclusively that there is an equilibrium reaction as well as the irreversible change in the case of the phenylisonitromethane, and since all of the curves belong to the same type, presumably also in the cases of the other substances.

In each case, as the change of conductivity due to the reversible reaction

becomes negligible, the rate of change of the conductivity becomes proportional to the conductivity, and this proportionality continues over the rest of the range of conductivities measured. This is shown by the linear portions of the curves.

If this phenomenon were due to a monomolecular change of an un-ionized substance to the true nitro compound or, to what is equivalent to this, a second-order reaction of the ions to the nitro compound, then a bend in the curve of $\log c$ against time (see Equation 2) should have been noticeable, unless the value of R is very much greater than the corresponding values for organic acids in aqueous solution; for, if in any case the acid were so weak that, throughout the range of concentrations measured, the amount of the substance ionized is negligible, then the conductivities would have fallen over a lower range than those measured. The values of R were measured for phenylisonitromethane and isonitromethane at 0° in the 50% methyl alcohol, and were found to be lower than those of acetic acid in aqueous solution at 0° .

$R = (c_{\text{sodium salt}} + c_{\text{HCl}} - c_{\text{NaCl}})/N$, where $c_{\text{sodium salt}}$, c_{HCl} and c_{NaCl} are the conductivities of the sodium salt of the nitro compound, of hydrochloric acid and of sodium chloride, respectively, all measured at the same very low concentrations. As all of these substances are strong electrolytes, 0.005 N is a low enough concentration for 10% accuracy. In the units in which the conductivities have been expressed in this paper, $c_{\text{HCl}} = 2.84$, $c_{\text{NaCl}} = 1$, c for the sodium salt of phenylnitromethane = 0.69 and c for the sodium salt of nitromethane = 0.90.⁴ Hence, $R = 506$ and 548 for phenylisonitromethane and isonitromethane, respectively.

With such values of R , the variations from apparently monomolecular curves, predicted by Equation 2, would have been noticed for acids which would give $\log c = -1.2$ when the concentration = 0.005 N . Since such a value of $\log c$ is less than those which would be obtained by extrapolating the linear portions of the curves to zero time, the first-order character of the curves cannot be attributed solely to monomolecular reactions of un-ionized molecules, nor to second-order reactions of ions.

On the other hand, if the linear portions of the curves are due to first-order reactions of the ions, the downward concavities of the curves demanded by Equation 1 could be obliterated by the upward concavities due to the reversible reactions, more especially, if the amounts of the true nitro compounds formed before the equilibrium reactions have become negligible are large. This would be the case if the nitro compounds are formed directly from the ions of the isonitro salt and not from those of the substances produced in the reversible reactions, for in that case the

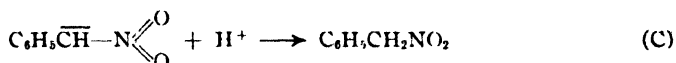
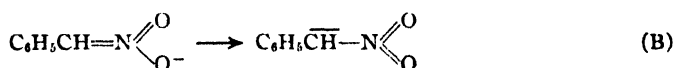
⁴ No correction has been made in these measurements for the hydrolysis of the salt, so that these figures are somewhat too high.

concentrations of the reacting ions at the beginning of the reactions are much higher than those corresponding to the steady state.⁵

Further, if there are any accompanying reactions of the un-ionized molecules, there would be a further obliteration of the downward concavities of the curves expected from Equation 1; but whatever the cause for the great range over which the curves are straight lines, the slopes of the lines at the lower concentrations must represent the rates of reactions which are first order with respect to the ions.

That the linear portion of the curve is to be attributed to a reaction monomolecular with respect to the negative ion was further verified in the case of nitromethane by Expt. 8. In this experiment excess of acid was used, which by its mass-action effect should reduce the rate of the reaction due to the negative ion. That this is the case is strikingly shown by a comparison of Curves 4 and 8.

The mechanism for these isomerization reactions shown by the rate measurements can be represented by the following equations, in which phenylnitromethane has been chosen as the substance depicted.



Equation A represents the reversible reaction which produces the first rapid change of conductivity, and which soon reaches a steady state. Equation B is the rate determining step of the changes which produce phenylnitromethane, and the reaction whose rate is measured by the slope of the linear portion of the curve, while Equation C is a rapid follow reaction, whose rate even in the most dilute solutions measured, must be great in comparison with that of the reverse of Reaction B.

It must be noted that rate measurements do not give direct evidence

⁵ This conclusion is supported by the fact that the extrapolations of the linear portions of the curve to zero time apparently do not give the true value of the ion concentrations corresponding to the steady state at initial total concentrations, for in the case of phenylnitromethane at 0° these values are not proportional to the square root of the initial concentrations, but seem to depend upon how quickly the steady state is reached; while in the case of the other two substances these extrapolations lead to higher values at lower temperatures, and the differences are greater than those which might be expected from changes in the value of *R* due to changes of temperature. This would mean that either the steady states are reached when the total concentrations of isonitro compounds are markedly less than the initial concentrations, or that the degree of ionization increases as the temperature decreases; this latter is unlikely, as generally the formation of a weakly ionized substance from ions is an exothermic process.

for the structural formulas of the substances involved, and that the formulas assigned to the substances involved in these equations are chosen only because they do not involve anomalous valences. While the authors

consider that the structures $\text{C}_6\text{H}_5\text{CH}=\text{N}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ and $\text{C}_6\text{H}_5\text{CH}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$

probably represent the negative ions of the sodium salt of phenylisonitromethane, and the substance formed by the reversible reaction, respectively, and that this latter substance is probably the isomer of phenylnitromethane which is precipitated from the salt with hydrochloric acid, they do not consider that the formula $\text{C}_6\text{H}_5\text{CH}^- - \text{NO}_2$ truly represents the negative ion which combines with hydrogen ion to form the true nitro compound. In the case of nitromethane, the heat of activation is so small (less than 10,000 cal.) that it seems very unlikely that it could represent the energy necessary to shift an electron from an oxygen to a carbon atom.

It may be noted that the formulation suggested for the reaction removes an anomaly which previously existed. Hantzsch, from his measurements, judged that the isonitromethanes were somewhat stronger acids than

acetic acid, but the suggested formula, $\text{RCH}=\text{N}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ would be ex-

pected to represent acids as strong as sulfurous acid, that is 1000-fold stronger than acetic acid because of the pentavalent nitrogen atom, while there is no reason to believe that the other formula suggested for isonitromethanes, namely, $\text{RCH}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$ which has neither double bonds

nor pentavalent nitrogen, would be as strong as acetic acid. However,

our experiments have shown that the original acid $\text{RCH}=\text{N}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ changes much too rapidly to permit of an estimate of its strength by such measurements as these, while the acidic properties of the substances $\text{RCH}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$, as shown by the marked conductivities after the steady

state has been reached, are due to its tautomeric equilibrium with the more acidic $\text{RCH}=\text{N}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}$ and not to its ionization to H^+ and $\text{RCH}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$

O^- . The over-all strength of the pseudo acids of the type $\text{RCH}-\text{N}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$

cannot be judged by extrapolation of the linear portions of the curves, as the values so obtained depend on the relative rates of the reactions

of Types A and B, as well as on the acidity of the intermediate compounds of the type $\text{RCH}-\text{N}-\text{OH}$.



In the cases of phenylnitromethane and *p*-nitrophenol, the final products of the reactions are indubitably the nitro compounds, as these substances can be obtained in large yields from their salts under more drastic conditions than those of these experiments. But nitromethane is much more sensitive to hydrolysis, and it was thought necessary to test experimentally whether the reaction which was measured is an irreversible hydrolysis or the formation of a pseudo acid from its salts, although Hantzsch has assumed it to be of the latter type. The following experiment with its result shows that Hantzsch's assumption is justified.

A 0.01 *N* solution of the sodium salt of isonitromethane was mixed with an equal volume of 0.01 *N* hydrochloric acid at 0°, and allowed to stand for 20 minutes. An equivalent of 0.01 *N* sodium hydroxide solution was then added, and again the solution was allowed to stand for 20 minutes. It was again mixed with an equivalent of 0.01 *N* hydrochloric acid and the conductivity was measured from time to time. The same solvent and the same precautions were used in this experiment as in the other measurements. The conductivity was found to decrease in the same way as in Expt. 4. The value of ϵ , 2.67 minutes after mixing, was 0.03, which is comparable with $\epsilon = 0.01$ after three minutes in Expt. 4, as the solution is only half as concentrated with respect to the isonitro acid in this experiment, owing to the double neutralization.

However, the final solutions obtained in the experiments on nitromethane gradually increase in conductivity on standing at 0°, but this change is slow compared to the changes of conductivity reported in this paper, and cannot produce significant errors.

The Velocity Constants and Heats of Activation

The velocity constants of the reactions are measured by the slopes of the linear portions of the curves, multiplied by 2.3 and divided by 60 to bring the units to reciprocal seconds. The values are given in Col. 3 of Table II. In each case they are the average values obtained from several independently drawn curves. They are velocity constants for the Type B reactions.

The heats of activation per mole of these same reactions are obtained from the rate constant measured at different temperatures by the usual equation, $Q = -R\Delta \ln k/\Delta(1/T)$, where k is the velocity constant and Q the heat of activation. The heats of activation in calories per mole are given in Col. 4 of Table II.

In Table II the values of B , another constant characteristic of reactions, are given in the last column. The logarithm of a monomolecular-reaction

constant may be expressed by the equation $\log_{10} k = B - Q/(2.3 \times RT)$. The reaction is thus determined by the constants B and Q .

TABLE II
VELOCITY CONSTANTS AND HEATS OF ACTIVATION

Substance	Temp., °C.	Velocity constant, sec. ⁻¹	Heat of activation per mole	B
Phenylnitromethane	5.2	1.78×10^{-4}	22000 ± 2000	13.56
Phenylnitromethane	0	8.34×10^{-5}		
Nitromethane	0	7.45×10^{-3}	8450 ± 600	4.66
Nitromethane	-23.8	1.68×10^{-3}		
<i>p</i> -Nitrophenol	-9.8	8.44×10^{-3}	4250 ± 800	1.47
<i>p</i> -Nitrophenol	-23.6	5.37×10^{-3}		

Inspection of Table II shows that Q and B vary widely for the different reactions. Q and B are both greatest for the slowest reacting substance, phenylnitromethane, and smallest for the fastest reacting substance, *p*-nitrophenol, and that B is large when Q is large. The differences in the Q 's and B 's for the various substances are more significant than a comparison of the rates, for the values of Q and B are such that if the reactions were carried out above 50°, the phenylnitromethane would be the fastest reacting of the three substances, and *p*-nitrophenol the slowest.

Addenda

In the body of the paper the equations

$$-d_i/dt = k_i \left(\frac{2c}{KR} + 1 \right) \quad (1) \quad -dc/dt = k_i' KR c^2 \left(\frac{2c}{KR} + 1 \right) \quad (2)$$

are given without derivation. The mathematical derivations are quite simple. The fundamental assumptions that the mobilities of the ions are constant and that the mass law is valid for the electrolytic dissociation may be expressed by

$$c = Ri \quad (3)$$

and

$$i^2/u = K \quad (4)$$

respectively, where i is the concentration of the ionized reactant, u that of the undissociated reactant, R is the proportionality constant between the concentrations of the ions and the conductivity of the solution due to the isonitro acid and K is the dissociation constant of the acid.

Since one mole of reactant forms one mole of resultant, the rate of formation of the resultant is equal to the rate at which the total reactant is used up, that is,

$$dx/dt = -d(i + u)/dt \quad (5)$$

where x is the concentration of the resultant.

Combining Equations 4 and 5 and eliminating u ,

$$dx/dt = -di/dt [(2i/K) + 1] \quad (6)$$

Now dx/dt depends upon the mechanism of the reaction, and for monomolecular reactions of the negative ion or of the undissociated acid,

$$dx/dt = ki \quad (7)$$

or

$$dx/dt = ku \quad (8)$$

Hence,

$$-di/dt = ki \left(\frac{2i}{K} + 1 \right) \quad \text{or} \quad -di/dt = k/K \cdot i^2 \left(\frac{2i}{K} + 1 \right)$$

Substituting c for i in these equations gives

$$-dc/dt = kc \left(\frac{2c}{KR} + 1 \right) \quad \text{and} \quad -dc/dt = k/KR \cdot c^2 \left(\frac{2c}{KR} + 1 \right)$$

When c is small, these equations become equivalent to the usual equations for monomolecular and dimolecular reactions, respectively.

In Expt. 8 excess of acid is present. If the concentration of the excess acid is called a , then Equation 4 becomes $i(i+a)/u = K$, while the other fundamental equations remain unchanged. Consequently $dx/dt = -(di/dt)[(2i/K) + (a/K) + 1]$ instead of $dx/dt = -(di/dt)[(2i/K) + 1]$. When i becomes very small compared to a , then $dx/dt = -di/dt[(a/K) + 1]$, so that if the reaction is monomolecular with respect to the ions, then

$$-di/dt = \left[k \left(\frac{a}{K} + 1 \right) \right] i, \quad \text{or} \quad -dc/dt = \left[k \left(\frac{a}{K} + 1 \right) \right] c.$$

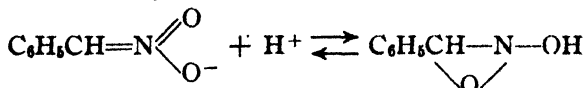
The reaction is thus still first order, but the constant is reduced from k to $k/[(a/K) + 1]$.

Summary

The isomerization of isonitromethane, phenylisonitromethane and *p*-isonitrophenol to the corresponding nitrocompounds has been investigated by measurements of the rates of the changes of electrical conductivity which occur when solutions of the sodium salts of these substances are mixed with hydrochloric acid.

In all these cases the rates of decrease of the conductivity were found to diminish very rapidly at first, and after some time were observed to become proportional to the conductivities, due to the isonitro compounds, and to remain so to as low values as it was possible to measure.

The twofold character of the curves corresponding to these results has been explained by assuming another type of isonitro compound which is formed by reversible reactions as, for instance, such a reaction as



The persistent proportionality between the rates of change of the conductivities and the conductivities of the isonitro acids has been taken as a strong indication that formations of the true nitro compounds occur through comparatively slow changes of the ions of the isonitro acids to

ions which combine rapidly with hydrogen ion to form the nitro compounds.

The velocity constants of these second reactions have been measured at two temperatures for each of the substances. The heats of activation of these reactions have been calculated from the results.

The heats of activation have been found to differ very markedly for the three substances, that for phenylisonitromethane being more than 10,000 cal. greater than that for nitromethane.

The heat of activation in the case of *p*-isonitrophenol has been found to be very small, being less than 5000 cal.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GOODYEAR TIRE AND RUBBER COMPANY]

RESEARCHES ON THIAZOLES. II. THE NITRATION AND REDUCTION OF 2-MERCAPTOBENZOTHIAZOLE AND ITS SUBSTITUTED DERIVATIVES

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In a previous paper¹ a new method of preparation for 2-mercaptobenzothiazole was given. This method was extended to the preparation of several new 2-mercaptobenzothiazoles which had hitherto not been described.

It is the purpose of the present paper to outline the results obtained by nitration and subsequent reduction of 2-mercaptobenzothiazole and its derivatives as given in the first paper.

Bogert² has shown that the nitration of 2-phenylbenzothiazole gives 6-phenyl-2-mercaptobenzothiazole. We were unable to fix the position of the nitro group in nitro-2-mercaptobenzothiazole by use of the procedure followed by Bogert. However, we were able to prove by another way that the nitro group is in Position 6.

The work of Kwaysser³ and Mylius⁴ has made available 2-amino-5-nitrothiophenol. After reduction this compound, treated with sodium hydrosulfide and carbon disulfide according to our previously described method gave 6-amino-2-mercaptobenzothiazole; m. p., 263°. The reduction product of nitrated 2-mercaptobenzothiazole after purification melted at 260°. A mixed-melting-point determination gave no decrease in melting point. We, therefore, conclude that on nitration the nitro group enters the ring in 2-mercaptobenzothiazole in Position 6.

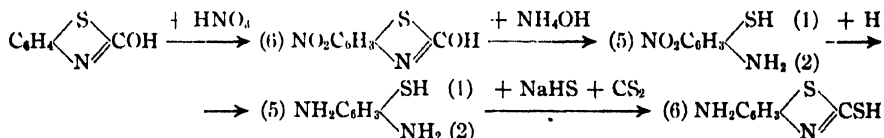
These reactions are

¹ Teppema and Sebrell, *THIS JOURNAL*, **49**, 1748 (1927)

² Bogert, *ibid.*, **44**, 826 (1922)

³ Kwaysser, *Ann.*, **277**, 240 (1893)

⁴ Mylius, *Dissertation*, University of Berlin, 1883.



Another amido-2-mercaptobenzothiazole, m. p. 216°, was described by us in our previous paper. From its method of preparation it must be 5-amino-2-mercaptobenzothiazole.

Attempts to prepare 5-nitro-2-aminothiophenol by fusion of the nitration product of 2-mercaptobenzothiazole were unsuccessful. Heating under pressure with aqueous ammonia gave 6-nitro-2-aminobenzothiazole.

By diazotization and Sandmeyer reaction of 6-amino-2-mercaptobenzothiazole the corresponding 6-chloro-2-mercaptobenzothiazole is formed. Benzaldehyde condenses readily with the amino group to give 6-benzal-amino-2-mercaptobenzothiazole.

A similar series of derivatives is formed by nitrating the 5-chloro-2-mercaptobenzothiazole. In this compound the position of the nitro group has not been definitely proved but it is believed to be in Position 6.

From 1,2,4-toluylenediamine and sulfur the corresponding disulfide was prepared according to Schultz and Beyschlag.⁵ By reaction with sodium hydrosulfide and carbon disulfide the 5-amino-6-methyl-2-mercaptobenzothiazole is produced. It gives all the reactions characteristic of an aminomercaptobenzothiazole.

In this paper the melting points given are uncorrected.

Experimental Part

6-Nitro-2-mercaptobenzothiazole.—Fifty g. of 2-mercaptobenzothiazole was dissolved in 250 g. of sulfuric acid, and a mixture of 40 g. of fuming nitric acid and 55 g. of concd. sulfuric acid was slowly dropped in while cooling the reaction mixture with ice and salt. The solution was stirred during the addition of the acid mixture. After all the nitric acid solution is added, the solution is stirred in the cold for one hour more. The solution is then poured onto ice, the precipitate filtered, washed with water and dried; yield, 63 g.; calcd., 65 g. By boiling this compound with aqueous ammonia and repeating this with the residue most of this nitration product could be brought in solution.

From the red solution thus obtained, a yellow precipitate was formed by the addition of dilute acid. After filtering and drying, this material was crystallized from glacial acetic acid, giving yellow needles; m. p., 255–257°.

Anal. Calcd. for $\text{C}_7\text{H}_4\text{O}_2\text{N}_2\text{S}_2$: S, 30.19; N, 13.20. Found: S, 29.94; N, 13.48.

The crude nitration product which is obtained by pouring the nitric acid solution into ice water is a mixture of nitro-2-mercaptobenzothiazole and its disulfide. Aqueous ammonia dissolves in the cold only the free mercaptan. When the residue was heated with aqueous ammonia it also dissolved and gave the same nitro compound on addition of acid.

This is a remarkable case of the influence of the nitro group on the stability of the sulfur-to-sulfur bond. Whereas the disulfide of 2-mercapto-

⁵ Schultz and Beyschlag, *Ber.*, **42**, 743 (1909).

benzothiazole does not give the free mercaptan easily by boiling with alkalis, introduction of the nitro group loosens the bond between the sulfur atoms.

Amido-2-mercaptobenzothiazole.—The reduction of nitro-2-mercaptobenzothiazole can easily be accomplished by sodium hydrosulfide.

Fifty g. of the nitro compound was suspended in a solution of 75 g. of sodium sulfide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, in 250 cc. of water which had previously been saturated with hydrogen sulfide. The mixture was then heated on a sand-bath under reflux for 24 hours while hydrogen sulfide was bubbled through the solution.

The solution was acidified with dil. acetic acid and heated on a steam-bath to complete the coagulation of the precipitate. The mixture of the amido compound and sulfur was filtered and the solid extracted with hot aqueous ammonia. Addition of dil. acetic acid yielded amido-2-mercaptobenzothiazole as a yellow-white precipitate which could be crystallized from aniline. It may also be purified by dissolving it in pyridine and reprecipitating with chloroform; m. p., 260° .

Anal. Calcd. for $\text{C}_7\text{H}_6\text{N}_2\text{S}_2$: S, 35.2; N, 15.35. Found: S, 34.82; N, 15.50.

This amino-2-mercaptobenzothiazole was diazotized as described below and coupled with β -naphthol. It gave a beautiful red dye.

The complete possibilities of utilizing the various amino-2-mercaptobenzothiazoles as intermediates in the synthesis of dyes have not been entirely developed. Further work is being done and will be reported in a separate communication.

A considerable improvement in the preparation of 6-amido-2-mercaptobenzothiazole could be made by omitting the isolation of the free nitro-2-mercaptobenzothiazole.

The crude nitration product of 2-mercaptobenzothiazole was reduced with sodium hydrosulfide and gave the corresponding amido-2-mercaptobenzothiazole in almost quantitative yield. It was purified as described above.

Position of Nitro Group.—The following experiments were carried out to prove the constitution of nitro-2-mercaptobenzothiazole, of which only the last method was successful.

(1) As already mentioned above, diazotized *p*-nitro-aniline did not react with amido-2-mercaptobenzothiazole according to the method described by Bogert² for amino-2-phenylbenzothiazole.

(2) The second method is the fusion of nitro-2-mercaptobenzothiazole with potassium hydroxide to give a nitro-aminothiophenol. However, through the formation of hydrogen sulfide during the fusion this compound seems to be reduced, and no definite compound could be isolated from the fusion.

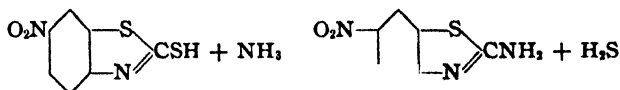
(3) To avoid the strong action of potassium hydroxide, the nitromercaptobenzothiazole was heated with concd. aqueous ammonia under pressure.

Three g. was heated with 40 cc. of aqueous ammonia (d, 0.95) for four hours at 160° . A red solution with crystals was obtained. The solution was filtered, diluted with twice

the amount of water and neutralized. The precipitate formed was unchanged nitro compound.

The residue on the filter was crystallized from alcohol and treated with bone black; yellow needles were obtained; melting point, 249°. It proved to be different from nitro-2-mercapto-benzothiazole, as mixed with this compound the melting point was 218°.

This compound is soluble in acid and insoluble in alkali. The yield under these conditions was small and most of the final product was unchanged nitro compound. The analysis for sulfur and nitrogen showed it to be 2-amido-6-nitrobenzothiazole, and its formation can be formulated as follows.



Anal. Calcd. for $\text{C}_7\text{H}_3\text{O}_2\text{N}_2\text{S}$: S, 16.41; N, 21.5. Found. S, 16.48; N, 20.75.

(4) A fourth method consists in the preparation of 5-nitro-2-oxybenzothiazole and treating this compound with aqueous ammonia according to Kwaysser³ to give 5-nitro-2-aminothiophenol. This compound is quite unstable when not dry, as it is easily oxidized to the corresponding disulfide.

It has been shown in a previous paper¹ that 2-mercaptobenzothiazole could be obtained from *o*-amidothiophenol with carbon disulfide in two ways. The new method described consisted in passing hydrogen sulfide, previously saturated with carbon disulfide, through an alkaline solution of the thiophenol.

This same procedure was applied to the reduction product of 5-nitro-2-amidothiophenol.

Reduction of 5-Nitro-2-amidothiophenol.—Four g. of 5-nitro-2-amidothiophenol was heated with 10 g. of granulated tin in 60 cc. of hydrochloric acid (1:1). The solution was boiled under reflux for three hours. The clear solution then obtained was diluted with much warm water and the tin precipitated with hydrogen sulfide. The filtrate from the tin sulfide was concentrated and neutralized with sodium hydroxide. Twenty g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was then added and hydrogen sulfide, previously saturated with carbon disulfide, was passed through the solution, which was kept at 80° for ten hours.

On acidification with dil. acetic acid a colorless precipitate was formed. This was filtered, redissolved in aqueous ammonia and reprecipitated with dil. acetic acid; yield, 3 g.

The dried material was crystallized from aniline; m. p., 263°. It was 6-amino-2-mercaptobenzothiazole.

Mixed with the reduction product of nitro-2-mercaptobenzothiazole, no decrease in melting point was observed.

The conclusion is, therefore, that the nitration of 2-mercaptobenzothiazole under the conditions mentioned yields 6-nitro-2-mercaptobenzothiazole.

2-Mercapto-6-benzalamidobenzothiazole.—Nine and one-tenth g. of 2-mercapto-6-amidobenzothiazole was suspended in 100 cc. of alcohol and 7.5 cc. of freshly-distilled benzaldehyde was added. After heating for one and one-half hours the reaction mixture consisted of yellow needles. By addition of more alcohol these crystals dissolved in the hot solution and, on cooling, light yellow crystals separated; m. p., 226°.

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}_2$: N, 10.37. Found: 10.13.

6-Chloromercaptobenzothiazole.—This compound was obtained from 6-amido-2-mercaptobenzothiazole by the well-known Sandmeyer reaction. As 6-amido-2-mercaptobenzothiazole is almost insoluble in water and does not form salts with acids, a modification of the usual way of diazotation was made. The following proved to be successful: 5 g. of 6-amido-2-mercaptobenzothiazole was dissolved in dil. sodium hydroxide (1:10) and this solution mixed with a solution of 3.8 g. of sodium nitrite in a little water.

The reason why twice the calculated amount of sodium nitrite is used is that part of the nitrous acid, set free, will oxidize the free mercaptan to its disulfide. In case the calculated amount of sodium nitrite is used, the diazotation will, therefore, be incomplete.

The solution was dropped slowly into 100 cc. of concd. hydrochloric acid, with ice cooling. If the solution was added carefully, the final solution did not contain any undissolved matter, but was slightly turbid. This solution was poured slowly into a dilute hydrochloric acid (1:1) solution of 12 g. of cuprous chloride, which was kept at 60–70°. A yellow-brown precipitate was formed. The reaction mixture was diluted with an equal volume of water and filtered, and the residue washed with water. The product obtained, being 6-chloro-2-mercaptobenzothiazole disulfide, was not isolated, but reduced with sodium hydrosulfide to the free mercaptan.

The solid, still wet, was mixed with 20 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 250 cc. of water, and hydrogen sulfide was passed through for four hours with heating. The final solution was filtered from a little dark colored solid and the filtrate acidified with dil. acetic acid. The precipitate was filtered and washed. It was freed from sulfur by dissolving in dilute aqueous ammonia and reprecipitating with dil. acetic acid. After being dried it was crystallized from aniline; m. p. (unsharp), 245°.

Anal. Calcd for $\text{C}_7\text{H}_4\text{NS}_2\text{Cl}$ Cl, 17.61. Found. 17.79.

Attempts to Obtain 6-Chloro-2-mercaptobenzothiazole by Chlorination of 2-Mercaptobenzothiazole.—When chlorine was passed through a solution of 2-mercaptobenzothiazole in carbon tetrachloride or *sym.*-tetrachloro-ethane, either at room temperature or at the boiling points of these solvents, no chlorinated 2-mercaptobenzothiazole was obtained.

In the first solvent only the disulfide of the mercaptan was formed. Chlorination in tetrachloro-ethane at the boiling point of this solvent gave an oil, b. p. 235–248°, with the characteristic odor of chlorophenyl mustard oil.

It was found, however, that 6-chloro-2-mercaptobenzothiazole is formed in a very small yield when 2-mercaptobenzothiazole reacts with chlorine in the presence of a small amount of iron.

Instead of 2-mercaptobenzothiazole, 2-mercaptobenzothiazole disulfide was used, as the latter product is produced as an intermediate compound. Ten g. of 2-mercaptobenzothiazole disulfide was dissolved in chloroform and 0.5 g. of iron powder added to the solution. Chlorine was passed through the boiling solution for five hours. After evaporation of the solvent at room temperature, the residue was extracted with chloroform to remove unchanged disulfide. The insoluble residue showed halogen present by qualitative test. The amount was small in comparison with unchanged disulfide.

One-half g. of this material was reduced with sodium hydrosulfide. A clear solution was obtained which, on acidification with dil. acetic acid, gave a white precipitate.

This compound was filtered, washed and redissolved in dil. aqueous ammonia. Dil. acetic acid precipitated a white material which, after filtering and drying, was crystallized from aniline, giving colorless needles; m. p., 230-235°. The amount of this compound was too small to be purified further.

To prove that it was identical with 6-chloro-2-mercaptobenzothiazole it was mixed with 6-chloro-2-mercaptobenzothiazole, m. p., 245°, previously obtained from 6-amino-2-mercaptobenzothiazole. The melting point was 235-240°, showing that it was identical with 6-chloro-2-mercaptobenzothiazole.

Nitro-5-chloro-2-mercaptobenzothiazole.—The same procedure as described for the nitration of 2-mercaptobenzothiazole was followed for 5-chloro-2-mercaptobenzothiazole.

Fifty g. of 5-chloro-2-mercaptobenzothiazole was dissolved in 175 cc. of concd. sulfuric acid and a mixture of 50 g. of fuming nitric acid and 70 g. of concd. sulfuric acid was dropped in gradually, cooling with ice and salt, while the solution was stirred mechanically.

After all of the mixed acid was added, stirring was continued for one hour and the mixture then poured into ice water. The yellow precipitate was filtered and digested with hot, aqueous ammonia. After repeating this thrice most of the nitro compound was dissolved and could be precipitated with acids, yield (dry), 50 g. It crystallized from acetic acid in yellow flakes; m. p., 190-192°.

Anal. Calcd. for $C_7H_4ClN_2O_2S_2$. N, 11.3, Cl, 14.4. Found. Cl, 14.30; N, 11.21.

Amido-5-chloro-2-mercaptobenzothiazole.—To prepare amido-5-chloro-2-mercaptobenzothiazole from nitro-5-chloro-2-mercaptobenzothiazole, sodium hydrosulfide could not be used as a reducing agent as it will not only reduce the nitro group but also substitute the chlorine atom to a certain extent.

Tin and hydrochloric acid were used as reducing agents. Fifty-five g. of nitro-5-chloro-2-mercaptobenzothiazole was added to a mixture of 100 g. of tin and 300 cc. of concd. hydrochloric acid. The solution was refluxed for four hours, whereby the yellow color of the suspended nitro-5-chloro-2-mercaptobenzothiazole disappeared. After dilution with water the solution was filtered and the residue digested with hot, aqueous ammonia.

The filtrate, acidified with dil. acetic acid, gave a white precipitate which crystallized from aniline, giving colorless needles; m. p., 240°.

Anal. Calcd. for $C_7H_6N_2S_2Cl$. S, 29.56; N, 12.93. Found: S, 29.17; N, 11.94.

Benzalamido-5-chloro-2-mercaptobenzothiazole. Two g. of amido-5-chloro-2-mercaptobenzothiazole was boiled with 50 cc. of alcohol and 2 cc. of benzaldehyde for one hour. The solution was treated with bone black and filtered hot. Yellow needles were obtained; m. p., 242°.

Anal. Calcd. for $C_{14}H_8N_2S_2Cl$. S, 21.01. Found: 21.02.

5-Amido-6-methyl-2-mercaptobenzothiazole.—This compound can easily be prepared from *m*-toluylenediamine disulfide.⁵

Thirty-five and one-half g. of *m*-toluylenediamine was dissolved in 284 cc. of alcohol and 18.5 g. of sulfur was added. The solution was heated under reflux on a water-bath for four hours. After distilling off the alcohol the residue was treated with a solution of

100 g. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 200 cc. of water which had been previously saturated with hydrogen sulfide and carbon disulfide. The mixture was heated on a sand-bath while hydrogen sulfide (saturated with carbon disulfide vapor) was bubbled through for five hours. The red solution was acidified with dil. acetic acid. First a sticky, yellow precipitate was formed, from which the remaining solution was decanted. On further acidification a white, flocculent precipitate was formed, which was filtered off and washed with water. The crude material was treated with aqueous ammonia, leaving the sulfur behind. The ammoniacal solution was acidified (cold) with dil. acetic acid. The precipitate formed was filtered, dried and crystallized from freshly distilled aniline; yield, 15.5 g.; m. p., 205–213°. It was further purified by crystallizing it twice from alcohol, raising the melting point to 220°.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{S}_2$: S, 32.65. Found: 32.84.

This 5-amido-6-methyl-2-mercaptobenzothiazole is a starting material for a new series of derivatives which contain a methyl group in Position 6 and any other substituent in Position 5.

5-Chloro-6-methyl-2-mercaptobenzothiazole.—Ten g. of 5-amido-6-methyl-2-mercaptobenzothiazole was dissolved in dil. sodium hydroxide solution and this was mixed with a solution of 7 g. of sodium nitrite in a little water. This solution is then dropped slowly into 200 cc. of concd. hydrochloric acid, with cooling. After standing for half an hour in ice water the diazotized solution was added slowly to a solution of 24 g. of cuprous chloride in hydrochloric acid solution ($1\text{HCl} \cdot 1\text{H}_2\text{O}$) which was kept at 60–70°. After all had been added the solution was diluted with an equal amount of water. The precipitate was filtered off, washed and dried. It was crystallized from dil. alcohol; m. p. (unsharp), 221–223°. The analysis indicates an impure product.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{NS}_2\text{Cl}$: S, 29.70; N, 6.49. Found: S, 30.64; N, 5.72.

Benzal-5-amido-6-methyl-2-mercaptobenzothiazole. Five and nine-tenths g. of 5-amido-6-methyl-2-mercaptobenzothiazole was dissolved in 100 cc. of alcohol, and 3.18 g. of benzaldehyde was added to the warm solution. After 2 minutes' heating the solution solidified. Much alcohol was added, but apparently the benzal compound is very difficultly soluble in alcohol. The suspension was refluxed for ten minutes more and then cooled and filtered; yield, 7.5 g. of colorless crystals, m. p., 253°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}_2$: S, 22.53; N, 9.86. Found: S, 22.48; N, 9.67.

Summary

1. The nitration products of 2-mercaptobenzothiazole and 5-chloro-2-mercaptobenzothiazole have been prepared and studied.
2. The position of the nitro group in nitro-2-mercaptobenzothiazole has been proved to be in the benzene ring in Position 6.
3. The reduction products of the above nitromercaptobenzothiazoles have been prepared, and from the amino compounds thus formed the aldehyde derivatives were prepared. By the Sandmeyer reaction the amino group was replaced by halogen.
4. From *m*-toluylenediamine disulfide a 5-amido-6-methyl-2-mercaptobenzothiazole was prepared. This gave also the corresponding aldehyde derivative, and by the Sandmeyer reaction the 5-chloro-6-methyl-2-mercaptobenzothiazole was obtained.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

THE ELECTRON-SHARING ABILITY OF ORGANIC RADICALS

BY R. M. HIXON AND I. B. JOHNS

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Ostwald¹ pointed out that certain elements or radicals, when substituted in organic acids, affected the dissociation constant in a uniform manner. Those elements, or radicals, which when substituted into acetic acid caused an increase in the dissociation constant, he called negative, and those which caused a decrease, positive. Wegscheider² summarizes the available data and puts them into a tabulated form from which it is possible to calculate the dissociation constant of various substituted acids. Many limitations to these generalizations, such as those of Bader³ and Hantzsch⁴ have been pointed out.

In 1901, Noyes and Lyon⁵ pointed out that if all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well must ionize into positive and negative parts. A few years later, Abegg⁶ stated that all elements are amphoteric, that is, exhibit both positive and negative electricity. We may interpret the generalizations of these pioneers to mean that the electron-sharing ability of any atom depends upon the strength of the other groups to which it is linked.

This generalization is involved in all of the recent theories⁷ which attempt to explain the distribution of affinity in the carbon compounds. All of these theories are qualitative in nature and the success of the manipulation depends upon reading into them a degree of stress or strain which can only be acquired by experience. The introductory statement used by Fry⁸ to one of his papers is especially significant. "The present series of papers is a further extension of the electronic principles of valence in an endeavor to interpret only a few of the many stereochemical problems now confronting us and concerning which Cohen tersely remarks: 'It must be confessed that we are still profoundly ignorant of the change which substituents effect in the character of the molecule as a whole, the causes which determine the rules of orientation-- and a host of other phenomena of a similar nature.' "

¹ Ostwald, *J. prakt. Chem.*, **31**, 433 (1885); *Z. physik. Chem.*, **3**, 170, 418 (1889).

² Wegscheider, *Monatsh.*, **23**, 287 (1902).

³ Bader, *Z. physik. Chem.*, **6**, 295 (1890).

⁴ Hantzsch, *Ber.*, **32**, 3071 (1899).

⁵ Noyes and Lyon, *THIS JOURNAL*, **23**, 460 (1901).

⁶ Abegg, *Z. anorg. Chem.*, **39**, 330 (1904).

⁷ A general summary of these theories is given by Henrich, Johnson and Hahn in "Theories of Organic Chemistry," John Wiley and Sons, New York, 1922, pp. 75-168.

⁸ Fry, *THIS JOURNAL*, **36**, 248 (1914).

The confusion is due mostly to the lack of a quantitative measure of the "electron-sharing ability" of the various carbon radicals. Derick⁹ attempted to establish such a standard by means of the acidic and basic dissociation constants of the various hydroxides. We may use the following electronic explanation for Derick's reasoning. (a) In water, hydrogen and oxygen are balanced. There is an equal tendency for the formation of hydrogen and hydroxyl ions. (b) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to take on an electron, the compound tends to ionize into $\text{RO}^- + \text{H}^+$. Furthermore, the degree of the ionization would be a measure of the "negativity" of R. (c) If one hydrogen is replaced by an element or radical R with a greater tendency than hydrogen to give up an electron, the compound tends to ionize into $\text{R}^+ + \text{OH}^-$. Furthermore, the degree of this ionization would be a measure of the "positivity" of R. He then uses the following mathematical value for these terms. Positivity = $-1000/\log K_{\text{basic}}$; negativity = $-1000/\log K_{\text{acidic}}$. Ostwald had previously considered this standard but had rejected it in favor of the standard mentioned above, based on acetic acid, because the "non-ionization" of such a large group of compounds makes this standard impossible to apply experimentally. For this very reason, Derick's treatment of the subject is limited to the organic acids.

An Activity Series of Organic Radicals.—This difficulty which limits the applicability of Derick's work can easily be avoided by the following reasoning. If the electron theory of valence holds, then the polar properties of any series of compounds such as $\text{R}(\text{OH})$, $\text{R}(\text{COOH})$, $\text{R}(\text{CH}_2\text{COOH})$, $\text{R}(\text{CH}_2\text{CH}_2\text{COOH})$, RNH_2 , RSH , $\text{RAsO}(\text{OH})_2$, etc., must be a function of the "electron-sharing ability" of R if we exclude from consideration under R all groupings which themselves have polar linkages.

An examination of all of the values given in Landolt-Bornstein for the dissociation constants of the acids and amines makes possible the comparison shown in Table I for the dissociation constants of $\text{R}(\text{NH}_2 \cdot \text{H}_2\text{O})$, $\text{R}(\text{COOH})$, $\text{R}(\text{CH}_2\text{COOH})$, $\text{R}(\text{CH}_2\text{CH}_2\text{COOH})$ and ROH .

Representative values from Table I are plotted in Fig. 1 against an arbitrary abscissa designated as "electron-sharing ability of various radicals." In plotting these results, it was observed that the curves were exponential no matter what units were chosen for the x axis. Accordingly, an arbitrary curve $y = \log K^{10} = -20(e^{0.05x} - 0.75)$ was drawn and the dissociation constants for the various amines $\text{R}(\text{NH}_2 \cdot \text{H}_2\text{O})$ were located on the curve, thereby fixing the position of R along the x axis. The corresponding values for the other derivatives of R were then located and a smooth

⁹ Derick, *THIS JOURNAL*, 33, 1152, 1162, 1181 (1911); 34, 74 (1912).

¹⁰ In Fig. 1 $y = \log K$. This value may be quickly approximated from the exponent given in Table I for the dissociation constant K .

TABLE I
DISSOCIATION CONSTANTS OF CORRESPONDING POLAR COMPOUNDS OF VARIOUS
RADICALS IN WATER AT 25°

Radical	Amine R NH ₂ H ₂ O	Acid R COOH	Acid R CH ₂ COOH	Acid R CH ₂ CH ₂ COOH	Hy- dride ROH
(CH ₃) ₃ C—	3 × 10 ⁻⁴	1 × 10 ⁻⁵			
CH ₃ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	
CH ₃ CH ₂ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	10 ⁻¹⁵
CH ₃ CH ₂ CH ₂ —	5 × 10 ⁻⁴	1 × 10 ⁻⁵	1 × 10 ⁻⁵	1 × 10 ⁻⁵	
CH ₃ CH=CHCH ₃ —	4 × 10 ⁻⁴	5 × 10 ⁻⁵	3 × 10 ⁻⁵		
C ₆ H ₅ CH ₂ —	2 × 10 ⁻⁵	5 × 10 ⁻⁵	2 × 10 ⁻⁵		
CH ₂ =CH—	6 × 10 ⁻⁵	6 × 10 ⁻⁵	4 × 10 ⁻⁵	2 × 10 ⁻⁵	
H—	2 × 10 ⁻⁵	2 × 10 ⁻⁴	2 × 10 ⁻⁵	1 × 10 ⁻⁵	10 ⁻¹⁴
C ₆ H ₄ CH ₃ - <i>p</i>	2 × 10 ⁻⁹	5 × 10 ⁻⁵			
C ₆ H ₄ OCH ₃ - <i>p</i>	6 × 10 ⁻⁹	3 × 10 ⁻⁵			
C ₆ H ₄ CH ₃ - <i>m</i>	6 × 10 ⁻¹⁰	5 × 10 ⁻⁵			
C ₆ H ₄ OCH ₃ - <i>o</i>	2 × 10 ⁻¹⁰	8 × 10 ⁻⁵			
C ₆ H ₅ —	3 × 10 ⁻¹⁰	7 × 10 ⁻⁵	5 × 10 ⁻⁵	2 × 10 ⁻⁵	10 ⁻¹⁰
C ₆ H ₄ CH ₃ - <i>o</i>	3 × 10 ⁻¹⁰	1 × 10 ⁻⁴			
C ₆ H ₄ Br- <i>p</i>	2 × 10 ⁻¹⁰				
C ₆ H ₄ Cl- <i>p</i>	1 × 10 ⁻¹¹	9 × 10 ⁻⁵			10 ⁻¹⁰
C ₆ H ₄ Br- <i>m</i>	9 × 10 ⁻¹¹	1 × 10 ⁻⁴			
C ₁ H ₇ - α	9 × 10 ⁻¹¹	2 × 10 ⁻⁴			
C ₇ H ₄ Cl <i>m</i>	6 × 10 ⁻¹²	2 × 10 ⁻⁴			
C ₆ H ₄ NO ₂ - <i>p</i>	1 × 10 ⁻¹²	4 × 10 ⁻⁴			10 ⁻⁸
C ₆ H ₄ NO ₂ - <i>m</i>	4 × 10 ⁻¹²	3 × 10 ⁻⁴			
H ₂ IC—		7 × 10 ⁻⁴	9 × 10 ⁻⁵	2 × 10 ⁻⁵	
C ₆ H ₄ Cl- <i>o</i>	9 × 10 ⁻¹³	1 × 10 ⁻³			10 ⁻⁹
CH ₃ CHCl—		2 × 10 ⁻³	9 × 10 ⁻⁵		
H ₂ CBr—		1 × 10 ⁻³	1 × 10 ⁻⁴	3 × 10 ⁻⁵	
H ₂ CCl—		1 × 10 ⁻³	9 × 10 ⁻⁵	3 × 10 ⁻⁵	
C ₆ H ₄ NO ₂ - <i>o</i>	1 × 10 ⁻¹⁴	6 × 10 ⁻³			
H ₂ C(NO ₂)—			2 × 10 ⁻⁴		
CH ₃ —C \equiv C—		3 × 10 ⁻³			
H ₂ C(CN)—		4 × 10 ⁻³			
C ₂ H ₅ OOC—			5 × 10 ⁻⁴	3 × 10 ⁻⁵	
HCCl ₂ —		5 × 10 ⁻²			
I—			8 × 10 ⁻⁴	9 × 10 ⁻⁵	
Br—			1 × 10 ⁻³	1 × 10 ⁻⁴	
Cl—			1 × 10 ⁻³	9 × 10 ⁻⁵	10 ⁻⁸
CN—			4 × 10 ⁻³		
NO ₂ —				2 × 10 ⁻⁴	

curve was drawn through them. It was found that the following mathematical expressions held for the dissociation constants of the various polar compounds listed.

$$R(NH_2 H_2O), y = \log K_1 = -20(e^{0.05x} - 0.75) \quad (1)$$

$$R(COOH), y = \log K_2 = 20(e^{0.5x-5.6} - 0.24) \quad (2)$$

$$R(CH_2COOH), y = \log K_3 = 20(e^{0.5x-6.6} - 0.24) \quad (3)$$

$$R(CH_2CH_2COOH), y = \log K_4 = 20(e^{0.5x-7.6} - 0.24) \quad (4)$$

Since the slope of the ROH curve is questionable, no equation has been derived.

For any reaction in which we start with the reactants at unit concentration and finish with the resultants at unit concentration, the thermodynamic expression $-\Delta F = RT \ln K$ or $-\Delta F = 2.3 RT \log K$ holds for the relationship between the "free-energy change" and the equilibrium constant. The application of this expression¹¹ to the present data will be as precise as the Ostwald dilution law. It would follow that the free energy of ionization of any polar derivative of the series of radicals

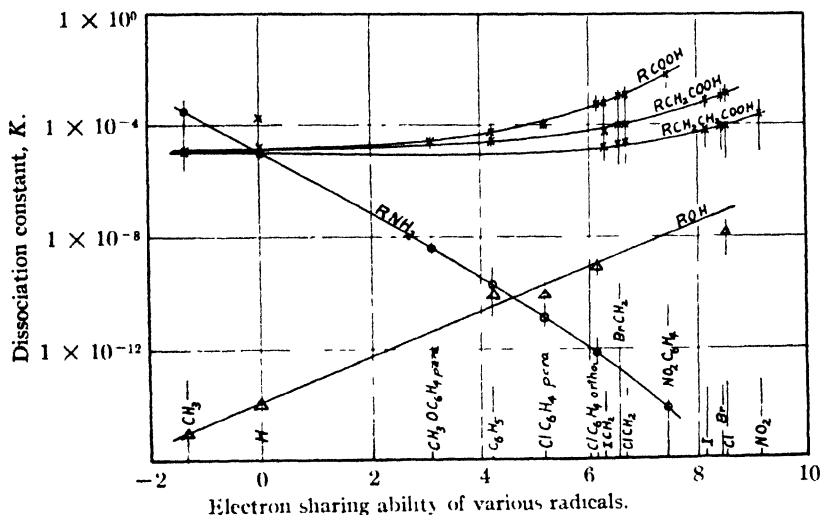


Fig 1.—Relation between the dissociation constants of different polar derivatives of various radicals.

R could be expressed as a function of the electron-sharing ability x ; for example,

$$R(NH_2 H_2O), \quad \Delta F = 46 RT(e^{0.5x} - 0.75) \quad (5)$$

$$R(COOH), \quad -\Delta F = 46 RT(e^{0.5x} - 0.24) \quad (6)$$

$$R(CH_2COOH), \quad \Delta F = 46 RT(e^{0.5x} - 0.24) \quad (7)$$

$$R(CH_2CH_2COOH), \quad \Delta F = 46 RT(e^{0.5x} - 0.24) \quad (8)$$

For each series this may be put into the general form

$$-\Delta F = k RT(e^{ax} - b - c) \quad (9)$$

from which may be derived the expression for x

$$x = \frac{1}{a} \ln \left(e - \frac{\Delta F}{kRT} \right) + \frac{b}{a} \quad (10)$$

The free-energy change represents the work required to separate by means of the hypothetical equilibrium box, one mole of the undissociated acid

¹¹ Acknowledgment is made to Professor Anson Hayes for suggesting this method of treating the "free-energy change."

or base into the normal solutions of the two respective ions. If this is expressed in electrical units, the number of faradays, nF , per mole will be unity in all of the above cases and the potential E only will vary. Equations 9 and 10 could then be written

$$E = \frac{kRT}{nF} (e^{ax-b} - c) \quad (11)$$

$$x = \frac{1}{a} \ln \left(c - \frac{EnF}{kRT} \right) + \frac{b}{a} \quad (12)$$

where E represents the potential of the ions of the normal acid or base and is the only variable in each series, the temperature being kept constant. It will be seen that E is an exponential function of the electron-sharing ability of the substituent group R . The term "electron-sharing ability" receives a mathematical expression but its mechanical significance is not clear. It is also apparent that the free energy of ionization, or the ionic potential of a member of any series can be calculated from the corresponding member of any of the other series; that is, combining Equations 5 and 6

$$\frac{-\Delta F_{\text{acid}}}{\Delta F_{\text{base}}} = \frac{F_{\text{acid}}}{-E_{\text{base}}} = \frac{e^{0.5x-5.6} - 0.24}{e^{0.05x} - 0.75} \quad (13)$$

The Effect of Intervening CH_2 Units upon the Properties of Polar Groups.—Derick has stated a "rule of thirds" for the relationship of the dissociation constants of the acids substituted in α , β , γ , δ positions. This generalization holds very well for the acids substituted by the strongly negative groups but does not hold for the less negative substituents.

TABLE II

OBSERVED AND CALCULATED VALUES FOR $-\log K$ OF SUBSTITUTED ACIDS WHEN VARIOUS SUBSTITUENTS "R" ARE REMOVED UNIFORM DISTANCES FROM THE CARBOXYL GROUP

The distance is measured by the number of intervening CH_2 units

	Intervening CH_2 units = s	R = (Cl)		R = (Br)		R = (I)		R = (CH_2Cl)		R = (CH_2Br)		R = (CH_2I)	
		Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
RCOOH	0	(0.4) ^a	0.21	(0.5) ^a	0.21	(1.0) ^a	0.80	2.81	2.85	2.86	2.85	3.12	3.12
RCH_2COOH	1	2.81	2.85	2.86	2.85	3.12	3.12	4.07	4.03	4.01	4.03	4.05	4.16
$\text{R}(\text{CH}_2)_2\text{COOH}$	2	4.07	4.03	4.01	4.03	4.05	4.16	4.52	4.57	4.58	4.57	4.64	4.62
$\text{R}(\text{CH}_2)_3\text{COOH}$	3	4.52	4.57	4.58	4.57	4.64	4.62	4.70	4.80	4.72	4.80	4.77	4.82
$\text{R}(\text{CH}_2)_4\text{COOH}$	4	4.70	4.80	4.72	4.80	4.78	4.82						
$\text{R}(\text{CH}_2)_5\text{COOH}$	6												
$\text{R}(\text{CH}_2)_6\text{COOH}$	8		5.00		5.00		5.00		5.00		5.00		5.00
		R = ($\text{C}_6\text{H}_5\text{OOC}-$)		R = (C_6H_5)		R = ($\text{CH}_2=\text{CH}$)		R = (CH_3)		R = (H)			
		Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.		
RCOOH	0	(1.70) ^a	1.80	4.16	4.10	4.25	4.23	4.73	4.80	3.67	3.52		
$\text{R}(\text{CH}_2)\text{COOH}$	1	3.35	3.56	4.28	4.46	4.42	4.50	4.84	4.82	4.73	4.70		
$\text{R}(\text{CH}_2)_2\text{COOH}$	2	4.52	4.36	4.64	4.66	4.68	4.66	4.81	4.84	4.84	4.94		
$\text{R}(\text{CH}_2)_3\text{COOH}$	3							4.80	4.85	4.81	4.95		
$\text{R}(\text{CH}_2)_4\text{COOH}$	4							4.84	4.86	4.80	4.97		
$\text{R}(\text{CH}_2)_5\text{COOH}$	6	4.84	4.96					4.84	4.88	4.84	4.98		
$\text{R}(\text{CH}_2)_6\text{COOH}$	8	4.85	5.00		5.00		5.00	4.95	4.92	4.84	5.00		

^a This value is extrapolated from the curves in Fig. 1.

The more general exponential Equation 9 fits all cases for which data are at present available.

Table II presents the measured and calculated values for $-\log K$ when various substituents "R" are removed uniform distances¹² from the carboxyl group, the distance being measured by the number of intervening CH_2 units.

Designating the number of intervening CH_2 units by z , the formulas used for the calculated values in Table II are as follows.

For	$\log K =$	For	$\log K =$
Cl	$20(e^{-0.8z-1.43} - 0.25)$	CH_2I	$20(e^{-0.8z-2.36} - 0.25)$
Br	$20(e^{-0.8z-1.43} - 0.25)$	$\text{C}_2\text{H}_5\text{OOC}$	$20(e^{-0.8z-1.83} - 0.25)$
I	$20(e^{-0.8z-1.56} - 0.25)$	C_6H_5	$20(e^{-0.5z-3.1} - 0.25)$
CH_2Cl	$20(e^{-0.8z-2.23} - 0.25)$	$\text{CH}_2=\text{CH}$	$20(e^{-0.4z-3.3} - 0.25)$
CH_2Br	$20(e^{-0.8z-2.21} - 0.25)$	CH_3	$20(e^{-z-4.6} - 0.25)$
		H	$20(e^{-1.6-2.6} - 0.25)$

These equations are of the same general form as Equations 1, 2, 3 and 4 and there would be the same general relationships between free energy of ionization and z as that expressed in Equation 10 for x

$$z = \frac{1}{a} \ln \left(c - \frac{\Delta F}{kRT} \right) + \frac{b}{a} \quad (14)$$

The equations developed can be combined to give a three-dimensional figure as shown in Fig. 2. The model for this photograph was constructed

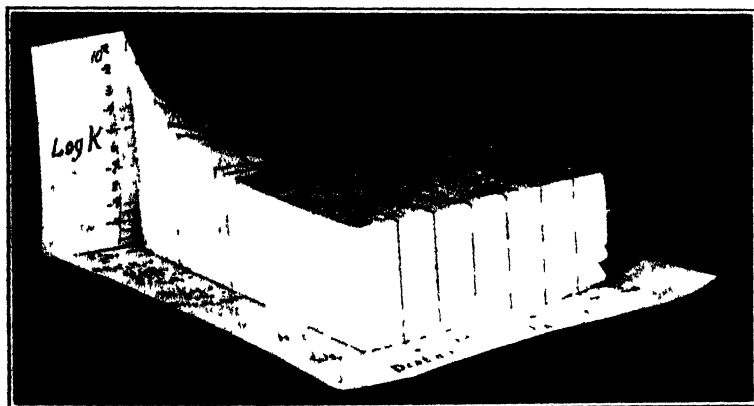


Fig. 2 —The systematic change in the dissociation constant of the acids as the substituting radical is moved varying distances, measured by number of intervening CH_2 units, from the carboxyl group

to scale from the equations already given, the location of the substituents R along the x -axis is the same as that in Fig. 1 and in fact the curve in the

¹² See discussion regarding this treatment under the heading, Surface Tension as a Measure of Polarity.

$x\gamma$ plane and the two succeeding curves are the same as those shown in Fig. 1 for the relationship between the dissociation constants of RCOOH , RCH_2COOH and $\text{RCH}_2\text{CH}_2\text{COOH}$. The only outstanding abnormality found so far is that of formic acid or the point where $\text{R} = \text{H}$. From the comparison between the homologous series of alkyl acids and amines given below, this would appear to be the characteristic "abnormality of the first member of the series." This is treated later.

From the mathematical relationship previously pointed out for the dissociation constants of the acids and amines, it would be expected that a plane similar to that shown in Fig. 2 for the dissociation constants of the acids could also be constructed for the corresponding amines.

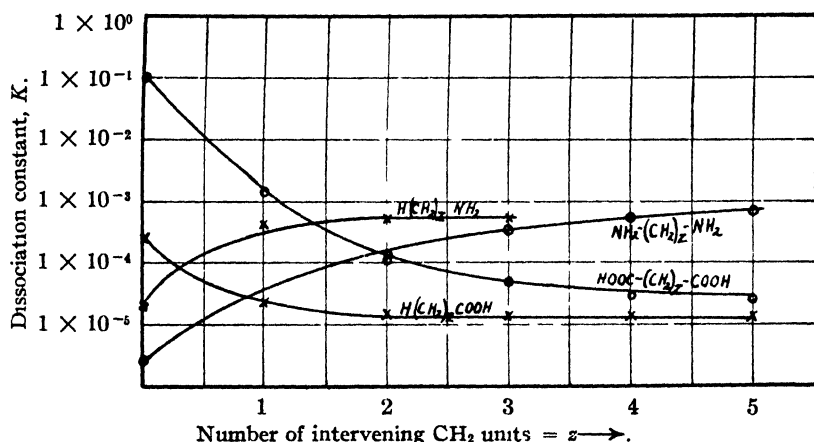


Fig. 3.—The similarity of the effect of intervening CH_2 units on the dissociation constants of corresponding acids and amines.

In fact the curves given in Fig. 1 for the two series RNH_2 and RCOOH would show the intersection of these surfaces with the $x\gamma$ plane. Unfortunately, data are not available for checking this conclusion over any extended range. However, the similarity of the change between the dissociation constants of the acids and amines as CH_2 units are interposed between R and the polar group is apparent from a comparison of the following pairs of equations for $\log K$ of

- (a) the alkyl amines $\text{H}(\text{CH}_2)_z\text{NH}_2$ $\log K = -20(e^{-1.6z-2.57} + 0.16)$
 the alkyl acids $\text{H}(\text{CH}_2)_z\text{COOH}$ $\log K = 20(e^{-1.6z-2.6} - 0.25)$
 (b) the alkyl diamines $\text{H}_2\text{N}(\text{CH}_2)_z\text{NH}_2$ $\log K = -20(e^{0.6z-2.05} + 0.15)$
 the alkyl diacids $\text{HOOC}(\text{CH}_2)_z\text{COOH}$ $\log K = 20(e^{0.6z-1.61} - 0.25)$

The similarity is more clearly seen by comparing the two pairs of curves in Fig. 3 for these equations. The agreement between the measured and calculated values is given in Table III for all except the alkyl acids, which were given in Table II.

OBSERVED AND CALCULATED VALUES FOR $-\log K$ OF SOME AMINES AND ACIDS

together in Table IV for comparison of effect of relative position. A perspective drawing is shown in Fig. 4, the substituting groups being spaced as to their electron-sharing ability on the same scale as in Figs. 1 and 2. The *ortho*, *meta* and *para* positions are plotted along the *z*-axis as of equal distance from the polar group, for the lack of any other standard. In spite of the rather large experimental error involved in the determination of these values, the only outstanding discrepancy is the value for the *p*-methylcarboxylic-substituted aniline.

Surface Tension as a Measure of Polarity.—The work of Langmuir¹⁸ regarding the structure of adsorbed films on the surface of liquids supports the generalizations advanced in this paper. After showing that the polar group causes orientation of the molecule in the surface film formed by an insoluble body on water, he calculated from Traube's data for the surface tensions of aqueous solutions of organic compounds, the loss in potential energy λ , when a gram molecule of the solute passes from the interior to the surface of the solution. Quoting from Langmuir, "... λ can be expressed in general by an equation of the form $\lambda_{\text{cal}} = \lambda_0 + 625 n$, where n is the number of carbon atoms in the molecule. The quantity λ_0 has a different value for each type of substance as is shown in Table V."

TABLE V
VALUES OF λ_0 GIVEN BY LANGMUIR

Type	Formula	λ_0	Type	Formula	λ_0
Tertiary alcohol	$R_3\text{COH}$	950	Ketone	RCOR'	295
Primary amine	RCH_2NH_2	600	Aldehyde	RCHO	210
Primary alcohol	RCH_2OH	575	Amide	RCONH_2	-510
Ester	RCOOR'	470	Dibasic acid (or alcohol)	..	-700
Monobasic acid	RCOOH	437			

In other words, the change for each intervening CH_2 unit is a constant, namely 625 calories, or all CH_2 units are equivalent. This would be the justification for treating the intervening CH_2 units as a measure of distance, as was done in Fig. 2.

A strict interpretation of Langmuir's equation implies that if λ were obtained for a number of radicals and plotted against intervening CH_2 units, as was done in Fig. 2 for the dissociation constants of the acids, a series of parallel planes would be obtained for all polar groups. It should be pointed out that the data available to Langmuir were limited almost entirely to the aliphatic compounds or, referring to Fig. 2, to that field in which there is little change in the potential of the polar group as CH_2 units are interposed between it and the radical R. If the orientation of the molecule is a function of the polar group, as Langmuir's work indicates, $\Delta\lambda$ for any homologous series would not be a constant unless the potential of this group remained unchanged as CH_2 units were inter-

¹⁸ Langmuir, *THIS JOURNAL*, 39, 1848 (1917).

posed. In Langmuir's data, there are only two series in which this can be checked, but both of these substantiate this modification of Langmuir's equation (see Table VI).

TABLE VI

COMPARISON OF THE POLARITY OF THE CARBOXYL GROUP AS MEASURED BY THE DISSOCIATION CONSTANT, AND THE EQUIVALENCE OF ALL CH_2 UNITS AS INDICATED BY LANGMUIR'S SURFACE-TENSION STUDY

Substance	Intervening CH_2 units	$-\log K$	Obs	$\Delta\lambda^a$
HCOOH	0	3.67	1078	632
HCH_2COOH	1	4.73	1710	
$\text{H}(\text{CH}_2)_2\text{COOH}$	2	4.83	2290	
$\text{H}(\text{CH}_2)_3\text{COOH}$	3	4.80	2910	580
HOOCCOOH	0	1.00	516	764
$\text{HOOC}(\text{CH}_2)\text{COOH}$	1	2.78	1280	
$\text{HOOC}(\text{CH}_2)_2\text{COOH}$	2	4.17	1510	230

^a This should be a constant equal to 625 calories, according to Langmuir's equation

If this limitation of Langmuir's generalization is found to hold over an extended range, it should offer an experimental means of explaining the discrepancies of the first member of each homologous series. It should be pointed out that our present theories of valence imply that affinity is a function of potential and structure only, the quantity factor entering only as multiple units. The application of any form of electrostatics indicates that such would not be the case and offers the best explanation for these "exceptions."

Summary

It is pointed out that if the electron theory of valence holds, the properties of any polar group must be a function of the "electron-sharing ability" of the radical or element to which it is linked. The available data are collected and the mathematical relationship is pointed out between the dissociation constants and free energy of ionization of the series $\text{R}(\text{NH}_2)$, $\text{R}(\text{COOH})$, $\text{R}(\text{CH}_2\text{COOH})$, $\text{R}(\text{CH}_2\text{CH}_2\text{COOH})$ and $\text{R}(\text{OH})$. It is also pointed out that an exponential equation of the same general form holds for the change in the dissociation constant as intervening CH_2 units are introduced. Theories of structure have been intentionally avoided since the mathematical relationships will hold, independent of the mechanical interpretations which may be advanced in explanation of them.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

POSITIVE HALOGENS ATTACHED TO CARBON IN THE AROMATIC SERIES. II. IODINE DERIVATIVES OF META-PHENYLENEDIAMINE AND OF RESORCINOL

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Some time ago one of us² called attention to the fact that certain compounds containing bromine or iodine in the benzene ring could undergo hydrolysis in such a way that the halogen was replaced by hydrogen, while the solution acquired oxidizing properties evidenced by the liberation of free halogen, or by the formation of more highly halogenated derivatives. Such behavior might be said to constitute the experimental definition of what is here meant by a positive³ halogen in organic combination.

In the cases previously cited, the halogen which reacted in this manner was always *ortho* or *para* to an amino or hydroxyl group. As these radicals are among the most strongly negative recognized by advocates of modern theories of polar valence⁴ as applied to organic compounds, the results are well in accord with those to be deduced from the electronic structure of benzene as depicted by Stieglitz⁵ or from the theory of induced alternations in polarity.^{6,7} As a further consequence of these theories

¹ The material here presented was used by John R. Sampey in partial satisfaction of the requirements for the degree of Doctor of Philosophy at the University of Chicago, 1923.

² Nicolet, *THIS JOURNAL*, **43**, 2081 (1921).

³ A *relatively* positive halogen (as shown by its reactions) is meant. The "assumption that each atom in a molecule exists in a definite oxidation-reduction stage which can be represented by an integral polar number" [Lewis, "Valence and the Structure of Atoms," A. C. S. Monograph Series, Chemical Catalog Co., New York, 1923] is here expressly denied. A displacement, probably relatively slight, of the electrons which in terms of the Lewis theory are shared by the atoms in question, could explain the results here described.

⁴ (a) Fry, "Electronic Conception of Valence," Longmans, Green and Co., London, 1921, p. 122. (b) Stieglitz, *THIS JOURNAL*, **44**, 1305 (1922). (c) Shoesmith, Hetherington and Slater, *J. Chem. Soc.*, **125**, 1314 (1924).

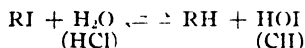
⁵ Ref. 4 b, p. 1293.

⁶ (a) Lapworth, *Mem. Manchester Phil. Soc.*, **64** [II], 1 (1920); (b) *J. Chem. Soc.*, **121**, 416 (1922). (c) Kermack and Robinson, *ibid.*, **121**, 427 (1922). (d) Lapworth and Shoesmith, *ibid.*, **121**, 1391 (1922).

⁷ It seems of interest to point out that since substituents entering the benzene ring are usually positive (Ref. 5) the data collected by de Lange [*Rec. trav. chim.*, **45**, 19 (1926)] on "The Displacement of Atoms and Groups in the Benzene Nucleus," can in general be interpreted as the replacement of *positive* groups. It will be shown in Paper V of the present series [Nicolet, *THIS JOURNAL*, **49**, 1810 (1927)] that the existence of reactions by which these polarities can be demonstrated may also be correlated with the possibility of the formation of quinoidal derivatives. Whatever the ultimate fate of the present interpretation may be, at the very least it constitutes a conspicuously efficient mnemonic system for the prediction of such replacements.

and of the interpretation previously given, it was to be expected that two amino or hydroxyl groups, both *ortho* or *para* to the halogens in question, would result in increased reactivity of these halogens in the sense indicated. It is the purpose of this paper to show that suitable iodo derivatives of *m*-phenylenediamine and of resorcinol behave in the anticipated manner.

The preparation of the necessary derivatives, a number of which are new, is described in the Experimental Part. All of them showed liberation of iodine when boiled with 10% hydrochloric acid, the rates varying both with constitution and with the solubilities of the individual substances. It was not thought desirable to estimate quantitatively the rates of iodine liberation, as these were obviously complicated by simultaneous reactions of resubstitution and of oxidation. While the *type* of these side reactions confirms the assumption that halogen is here removed in positive form, their *existence* would make useless any figures on rate of accumulation of oxidizing substances in solution. The type of initial reaction assumed is here indicated.



Data are presented showing relative rates of formation of iodide ion when the substances described are boiled with acid in the presence of sufficient acetic acid to dissolve them, and of an excess of stannous chloride, to prevent oxidation and resubstitution. The use of stannous chloride in the estimation of the positivity of halogens under such conditions has already been suggested.¹ Experience seems to have justified its use.⁸ The use of hydriodic acid as reducing agent in such tests has recently become somewhat common.⁹ While we are inclined to believe that the rate of removal of halogen atoms by reduction with hydriodic acid is probably related to the positivity of the halogen in question, there are few halogens which are not replaced by hydrogen under the influence of hydriodic acid at higher temperatures;¹⁰ there is also the further disturbing factor, particularly in the work quoted,⁹ that the reaction¹¹

⁸ Three lines of evidence may be mentioned. (a) The halogens removed, as recorded in chemical literature and as found in these experiments, are those, and only those, whose removal would be predicted on the basis of the theory here presented. (b) No evidence is known that stannous chloride can act like certain metals (in other words, magnesium in the Grignard reagents) to form an intermediate compound of a type which would be expected to hydrolyze in such a way as to give the results obtained. Burton and Kenner [*J. Chem. Soc.*, 121, 680 (1922)] suggest the formation of an intermediate compound which they assume would act in this way; we doubt their interpretation, for reasons given in this note, particularly under (c). (c) In certain analogous cases, evidence has been obtained (as yet unpublished) that the *rate* of removal of halogen is not proportional to the concentration of stannous chloride present.

⁹ Ref. 6 d. Shoesmith, *J. Chem. Soc.*, 123, 2828 (1923). Ref. 4 c.

¹⁰ Klages, *J. prakt. Chem.*, [2] 61, 307 (1900).

¹¹ Conant, Kirner and Hussey, *THIS JOURNAL*, 47, 488 (1925), and earlier papers there cited.

$\text{RBr} + \text{HI} = \text{RI} + \text{HBr}$ continually changes, to an uncontrolled extent, the nature of the halogen being removed. We are, therefore, much inclined to prefer stannous chloride as a diagnostic reagent. Its rather extreme specificity will be further illustrated in Paper IV of this series.

Experimental Part

4-Iodoresorcinol.¹²—It was not found possible to prepare this substance by the method of Stenhouse.¹³ Several attempts to modify his conditions led also to mixtures in which, after benzylation, it was possible to identify only derivatives of resorcinol and di-iodoresorcinol. The action of iodine chloride in ether, acetic acid or hydrochloric acid gave similar results. Attempts to obtain it from 5-iodo-2,4-dihydroxybenzoic acid or from 4-iodo-3-hydroxyphenyl benzoate also failed. Finally, mono-mercurized resorcinol was prepared by the method of Dimroth;¹⁴ the yield was very poor. Replacement of the mercury by iodine took place normally, and Stenhouse's 4-iodoresorcinol¹⁵ resulted.

4,6-Di-iodoresorcinol.—To 5 g. of resorcinol dissolved in 185 cc. of 20% hydrochloric acid was added 7.3 g (2 moles) of iodine monochloride. A precipitate appeared immediately. After fifteen minutes, the excess of iodine was removed with sodium sulfite, the solution filtered, and the solid dried and crystallized from benzene; yield, 80%. The substance forms colorless crystals, m. p. 145°, readily soluble in ether, alcohol and benzene, less so in chloroform and hot water, and nearly insoluble in cold water and ligroin.

Anal. (Carius). Calcd. for $\text{C}_6\text{H}_4\text{O}_2\text{I}_2$: I, 70.1. Found: 69.9.

The same substance was also made by the method of Stenhouse¹³ but a pure product was more difficult to obtain by this procedure.

4,6-Di-iododibenzoylresorcinol.—The di-iodoresorcinol was dissolved in 10% sodium hydroxide solution, and benzyolated by the Schotten-Baumann method. The product decomposed at 195–200°.

Anal. (Carius). Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_4\text{I}_2$: I, 44.6. Found: 45.0.

4-Iodo-3-hydroxyphenyl Benzoate.—Monobenzoylresorcinol¹⁶ was dissolved in glacial acetic acid, and treated with 1 mole of iodine chloride in the same solvent, avoiding rise in temperature. After 15 minutes water was added and the excess of iodine was removed with sodium sulfite. The insoluble material (yield, 65%) was crystallized from benzene. It decomposed at 153–155°.

Anal. (Rosanoff).¹⁷ Calcd. for $\text{C}_{13}\text{H}_9\text{O}_3\text{I}$: I, 37.3. Found: 37.4.

5-Iodo-2,4-dihydroxybenzoic Acid.—Resorcinic acid¹⁸ was iodinated with one mole

¹² No proof is here offered as to the positions assigned to iodine in the products described. The structures given seem logical and further work in progress appears likely to confirm them.

¹³ Stenhouse, *Ann.*, **171**, 311 (1874).

¹⁴ Dimroth, *Ber.*, **35**, 2865 (1902).

¹⁵ Richter, "Lexikon der Kohlenstoff-Verbindungen" gives 167° as the melting point of this substance. That given by Stenhouse (67°) is correct.

¹⁶ Kauffmann and Kugel, *Ber.*, **44**, 753 (1911).

¹⁷ Drogin and Rosanoff, *THIS JOURNAL*, **38**, 711 (1916).

¹⁸ Bistrzycki and Kostanecki, *Ber.*, **18**, 1984 (1855).

of iodine monochloride in ether solution. The product (yield, 44%), after crystallization from dilute acetone, melted at 172°. Attempts to prepare it by the method of Stenhouse¹³ gave a mixture of mono- and di-iodinated acids.

Anal. (Carius). Calcd. for $C_7H_5O_4I$: I, 45.4. Found: 45.7.

3,5-Di-iodo-2,4-dihydroxybenzoic Acid.—To a solution of 11 g. of resorcinic acid and 36 g. (2 equivalents) of iodine in 100 cc. of ether, was added 75 g. of litharge, and the whole was refluxed for two hours. After evaporation of the ether, the residue was extracted with alcoholic alkali, and the crude di-iodo acid recovered from the extract by dilution with water, acidification and treatment with sodium sulfite; yield, 50%. The product decomposed at 193–196°.

Anal. (Carius). Calcd. for $C_7H_3O_4I_2$: I, 62.3. Found: 62.9.

4-Chloro-6-iodo-*m*-phenylenediamine.—4-Chloro-*m*-phenylenediamine was iodinated in cold, absolute methyl alcohol solution with 1 mole of iodine and an excess of litharge. After three hours, the solution was filtered, the residue washed with methyl alcohol and the product recovered from the combined filtrates by dilution with water; yield, 80%; m. p., 98°.

Anal. (Carius). Calcd. for $C_6H_6N_2ClI$: AgCl, AgI, 140.2. Found: 139.9.

The same substance was obtained by refluxing a mixture of the chlorodiamine and iodine with water, ether and calcium carbonate. The yield, however, was less good. Iodination with iodine monochloride was unsatisfactory, as oxidation of the amine occurred.

4-Iododiacetyl-*m*-phenylenediamine.—*m*-Nitro-acetanilide was reduced with iron and acetic acid.¹⁹ The solution was filtered from the excess of iron and tarry impurities before making alkaline with sodium carbonate. After salting out and filtering, repeated extraction of the solid with hot benzene gave 70% of the calculated quantity of *m*-amino-acetanilide. Into 5 g. of this, dissolved in 200 cc. of 5% hydrochloric acid, was slowly aspirated 4.9 g. (1 mole) of iodine chloride as vapor. The crude iodo-mono-acetyldiamine was dried, and triturated in a mortar with 2 g. of fused sodium acetate and 3 cc. of acetic anhydride, to form the diacetyl derivative. After crystallization from benzene and from chloroform, the 4-iododiacetyl-*m*-phenylenediamine decomposed at 175–180°.

Anal. (Carius). Calcd. for $C_{10}H_{11}O_2N_2I$: I, 35.5. Found: 36.0.

4,6-Di-iodo-3-acetylamino-aniline.—Four g. of *m*-amino-acetanilide was dissolved in 200 cc. of warm 10% hydrochloric acid, and 8 g. (2 equivalents) of iodine chloride was added. After 15 minutes, sodium sulfite was added to remove the excess of iodine and then sufficient caustic alkali to liberate the amine. The product, crystallized from methyl alcohol, melted at 172–174°.

Anal. (Carius). Calcd. for $C_8H_8ON_2I_2$: I, 60.6. Found: 60.5.

Method of Hydrolysis and Analysis.—All of the substances which have been described liberate iodine when boiled with hydrochloric acid. Some, however, are only slightly soluble in this reagent. Moreover, the iodine liberated causes variable amounts of resubstitution and of oxidation. It was therefore decided to measure the reactivity of iodine in the respective substances by adding sufficient acetic acid to bring them into solution and also an excess of stannous chloride to remove the liberated iodine (as iodide ion) from further reaction. The procedure was as follows.

¹⁹ By the method used for the *para* compound by Nietzki, *Ber.*, 17, 343 (1884).

The halogen compound (0.125 g) was dissolved in 10 cc. of hot glacial acetic acid. To this solution, heated in a bath of boiling water, was added 5 cc. of a hot solution containing 10% each of hydrochloric acid and of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Heating was then continued for the time desired, and the solution was removed from the bath, rapidly cooled in water, and analyzed for iodide.

The analytical procedure was based on a method of Fresenius²⁰ and may be thus outlined.

To the sample to be analyzed, 15 cc. of chloroform was added. Then a 10% solution of sodium nitrite was added, drop by drop, with thorough mixing until the chloroform layer began to be colored; an additional 0.5 cc was then added; the chloroform was separated and the solution extracted with two more 15cc. portions of chloroform. The combined chloroform extracts were then washed with several small portions of water. After the addition of a few drops of sodium bicarbonate solution, the iodine in the chloroform layer was titrated with 0.02 *N* sodium thiosulfate solution. Special tests in each case showed that the action of nitrous acid under the conditions described did not liberate disturbing amounts of iodine from any of the organic substances used

TABLE I
RELATIVE RATES OF IODINE REPLACEMENT

Compound used	Time of reaction, minutes	Total iodine removed, %
4-Iodoresorcinol	5	87
4,6-Di-iodoresorcinol	7	66.8
	7	66.5
4-Iodo-3-hydroxyphenyl benzoate	30	11.6
	60	20.0
4,6-Di-iododibenzoylresorcinol	60	2.5
	60	2.7
5-Iodo-2,4-dihydroxybenzoic acid	30	42.4
3,5-Di-iodo-2,4-dihydroxybenzoic acid	30	39.8
4-Iodo- <i>m</i> -phenylenediamine ^a	5	66.8
	5	66.0
4,6-Di-iodo- <i>m</i> -phenylenediamine ^{a,b}	5	86.6
	5	85.5
4-Iododiacetyl- <i>m</i> -phenylenediamine	20	66.0
4-Iodo-6-chloro- <i>m</i> -phenylenediamine	5	98.0
	5	97.5
2-Iodo- <i>p</i> -phenylenediamine ^c	60	25.6
	60	25.2
3-Iodo-4-aminotoluene	30	22.0

^a The corresponding acetyl derivatives were heated for two hours with an excess of 3% sodium hydroxide in 80% alcohol, and the solution was filtered hot to remove a small amount of tar. Water was then added and the alcohol removed by distillation. After cooling, white crystals remained which were separated and dried.

^b Morgan and Wootton [*J. Chem. Soc.*, **87**, 938 (1905)] have described this substance. They found it rather unstable, and state that "the hydrochloride is decomposed by boiling water."

^c We are indebted to Dr. W. L. Ray for a sample of this compound.

²⁰ Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, New York, vol. 2, 1919, p. 657.

Relative Ease of Removal of Iodine.—The conditions used have been described. Table I gives the percentage of total iodine present removed after heating at 100° for the lengths of time specified.

Summary

1. The preparation of a number of new iodo derivatives of resorcinol and of *m*-phenylenediamine has been described.
2. A standard method for the removal of iodine from these substances by hydrolysis and mild reduction has been applied and the results have been correlated with the theory presented as to the relatively positive nature of the halogens involved.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

POSITIVE HALOGENS ATTACHED TO CARBON IN THE AROMATIC SERIES. III. DERIVATIVES OF PARA-PHENYLENEDIAMINE, PARA-NITRO-ANILINE AND MESITYLENE

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As has been more clearly set forth in previous papers² a positive character is attributed to such halogens as are removed on hydrolysis to give products other than halides, and are replaced during this reaction by hydrogen. Such behavior has been demonstrated in the case of a number of *o*- or *p*-bromo or iodo derivatives of phenol and of aniline, and corresponding iodo derivatives of resorcinol and of *m*-phenylenediamine have been shown to give similar results with the greater readiness which would be expected if the two negative groups united in enforcing an increased positivity of the halogens in question.

Before reporting the work done with derivatives of *p*-phenylenediamine and *p*-nitro-aniline, some results obtained with iodomesitylene will be discussed briefly. The methyl group is usually considered to be negative, although conspicuously less so than the hydroxyl or amino group. A sufficient number of methyl groups, properly placed, might perhaps cause an iodine atom to show properties similar to those referred to above. The ideal derivative for such a purpose should be iodomesitylene,³ which

¹ The material here presented was used by William L. Ray in partial satisfaction of the requirements for the degree of Doctor of Philosophy at the University of Chicago, 1923.

² (a) Nicolet, *THIS JOURNAL*, **43**, 2081 (1921). (b) Nicolet and Sampcy, *ibid*, **49**, 1796 (1927).

³ Klages [*J. prakt. Chem.*, [2] **61**, 307 (1900)] has shown that iodomesitylene is reduced by hydriodic acid at a considerably lower temperature than that required for iodobenzene. Töhl and Eckel [*Ber.*, **26**, 1099 (1893)] found that iodomesitylene yielded

contains three methyl groups, all *ortho* or *para* to the iodine in question. It was found that while a solution of iodomesitylene in glacial acetic acid containing hydrogen chloride could be heated under reflux without the liberation of appreciable quantities of iodine, such solutions, when heated in sealed tubes at 135 or 150°, showed iodine liberation to a very considerable extent. Under similar conditions phenyl iodide showed, as was expected, no evidence of reaction.

Preparation and Hydrolysis of Iodomesitylene.—The iodination of mesitylene with iodine and iodic acid in acetic acid solution⁴ gave better results than the use of sulfur iodide.⁵ Owing to the insolubility of iodomesitylene in water, a solution was prepared containing, per 100 cc. of glacial acetic acid, 5.6 g. of iodomesitylene and 6.6 g. of dry hydrogen chloride. Portions of this solution were heated in sealed tubes in a bomb furnace with the results shown in Table I. The liberated iodine was titrated with thiosulfate, and unaltered iodomesitylene was recovered in each case. After the last run no di-iodomesitylene could be found, showing that resubstitution had not occurred to any appreciable extent. Mesitylene was, however, isolated and identified by its boiling point and by the deep red color it gave with diazotized picramide.⁶

TABLE I
LIBERATION OF IODINE FROM IODOMESITYLENE

Time of heating, hours	Temp., °C.	Total iodine liberated, %
1	135	7.8
1	135	9.5
4.5	150	20.0
6	150	42.9

Iodobenzene was heated under conditions parallel to those described. No iodine color developed and no benzene could be detected.

A solution of 2 g. of iodomesitylene and 3.66 g. (2 molecular proportions) of stannous chloride in 7.2 cc. of concd. hydrochloric acid and 34 cc. of acetic acid was heated for 6.5 hours at 135°. The chief product was mesitylene, although a little of the iodo derivative remained.

As a test of the theory as to the importance of the position occupied by the activating groups, as well as of their number and character, it was considered desirable to study the effect on the lability of a bromine or iodine atom in the 2 position relative to an amino group, of additional substituents such as an amino or a nitro group in the 4 position. To this end, suitable derivatives of *p*-nitro-aniline and of *p*-phenylenediamine were prepared and characterized.

di-iodomesitylene when shaken with concd. sulfuric acid. The latter is, however, too strong an oxidizing agent to make this resubstitution conclusive evidence of positivity.^{2a}

⁴ Klages and Storp, *J. prakt. Chem.*, [2] 65, 564 (1902).

⁵ Edinger and Goldberg, *Ber.*, 33, 2881 (1900).

⁶ Meyer and Tochtermann, *Ber.*, 54, 2283 (1921).

Hydrolyses with Acid Only.—Solutions of the substance in 10% hydrochloric acid were boiled under reflux for suitable periods. After appropriate adjustment of the acidity, these solutions were then titrated with thiosulfate. The results obtained with 2-iodo-4-nitro-aniline are given in Table II, with velocity constants (time in minutes) calculated for a first-order reaction.

TABLE II
HYDROLYSIS OF 2-iodo-4-NITRO-ANILINE WITH ACID ONLY

Time, min.	Reaction, %	$K \times 10^3$
120	27.6	2.69
205	45.7	2.98
240	51.2	2.99
360	63.3	2.82

The "constants" obtained by this method have, however, relatively little meaning and are given only to illustrate this fact. The accumulation of oxidizing power in the solution (which is what is measured) really represents the difference between hydrolysis on the one hand and resubstitution or oxidations of other types on the other. In the case of iodophenylenediamine, extensive oxidation was evident from the first and the values found were very irregular. With iodonitro-aniline no destructive oxidation was noticed. The extent to which resubstitution took place is unknown, at least no di-iodonitro-aniline could be detected under the conditions described. When, however, iodonitro-aniline was heated under reflux with three parts of glacial acetic acid and one of hydrochloric acid, some 2,6-di-iodo-4-nitro-aniline (m. p., 243°) was isolated, and when 2 g. of the iodonitro-aniline was heated with 20 cc. of concd. hydrochloric acid in a bomb tube for eight hours at 105° , not only was some of the di-iodo derivative formed, but the resulting solution showed very little oxidizing power. In view of the other results described, there can be little question that hydrolysis was here a fairly rapid reaction, but resubstitution must have taken place with almost equal efficiency. The reason for placing little weight on quantitative results obtained in the presence of acid alone is thus apparent.

Hydrolyses in the Presence of Stannous Chloride.—This more accurate method cannot, of course, be applied to nitro compounds, as they would undergo reduction. In making measurements, 2 g. of substance was dissolved in 20 cc. of 10% hydrochloric acid containing 4.0 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Such solutions were boiled under reflux for the desired periods, and then cooled. Iodine was determined as described by Nicolet and Sampey.^{2b} The results obtained with 2-iodo-*p*-phenylenediamine are given in Table III, together with the velocity constants calculated on the assumption⁷ that the reaction rate is proportional only to the concentration of the

⁷ For a justification of this assumption, see Ref. 2b.

organic iodo compound. For comparison, *o*-iodo-aniline was prepared and hydrolyzed under parallel conditions. The percentage of reaction after 15 and 30 minutes was in this case 61.9 and 89.0%, corresponding to $K \times 10^3 = 64.0$ and 74.0, respectively. It is apparent that the 4-amino group decreases the rate of reaction decidedly.

TABLE III
HYDROLYSIS OF IODO-*p*-PHENYLENEDIAMINE, USING STANNOUS CHLORIDE

Time, min.	Total iodine removed, %	$K \times 10^3$, min.
60	29.4	5.9
180	72.9	7.2
240	79.4	7.1
300	89.5	7.5

The hydrolysis of bromo-*p*-phenylenediamine was similarly carried out in the presence of stannous chloride, but the direct determination of small quantities of bromine in the resulting solutions offered too great difficulties, and the progress of reaction was followed in a somewhat rough manner as follows.

After heating for the desired lengths of time, the solutions were cooled, treated with an excess of sodium acetate to remove free hydrochloric acid and then well shaken with 25 cc. of acetic anhydride. The precipitates, consisting of a mixture of the diacetyl derivatives of *p*-phenylenediamine and its bromo derivative, with base tin salts, were collected, and the tin salts washed out with dil. hydrochloric acid. Bromine was then determined (Carius) in the residue, and the proportion of the bromo compound calculated. As diacetyl *p*-phenylenediamine is decidedly less soluble than its bromo derivative, this method somewhat exaggerates the ease of bromine removal. After boiling for six and nine hours the extent of bromine removal was found to be 54.3 and 78.8%, corresponding to values of $K \times 10^3$ (minutes) of 2.3 and 2.9, respectively. As anticipated, bromine is removed less rapidly than iodine.

Experimental Part

2-Iodo-*p*-phenylenediamine.—Ten g. of 2-iodo-4-nitro-aniline⁸ was covered with 50 cc. of concd. hydrochloric acid and gently warmed, and 30 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 50 cc. of hydrochloric acid was added slowly with stirring. Stirring and warming were continued until most of the material was dissolved and the yellow color had disappeared. The solution was cooled in ice (a white double salt separated) and cautiously made alkaline with 50% sodium hydroxide solution. After thorough cooling, rapid filtration gave a 75% yield of product which crystallized from water in white needles; m. p., 110.5°.

Anal. (Carius). Calcd. for $\text{C}_6\text{H}_7\text{N}_2\text{I}$: I, 54.24. Found: 54.03, 53.93.

2,5-Diacetyl-amino-iodobenzene.—This was readily obtained by the action of acetic anhydride and crystallized from acetic acid; m. p., 211.5°.

Anal. (Carius). Calcd. for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2\text{I}$: I, 39.91. Found: 39.80.

2,5-Dibenzoylamino-iodobenzene.—The base was benzoylated by the Schotten-Baumann method. The product, slightly soluble in the commoner solvents, was crystallized from nitrobenzene; m. p., 254°.

⁸ Willgerodt and Arnold, *Ber.*, **34**, 3351 (1901).

Anal. (Carius). Calcd. for $C_{20}H_{16}O_2N_2I$: I, 28.71. Found: 28.86.

Acetylation of 2,6-Di-iodo-4-nitro-aniline.—Körner and Contardi⁹ reported an acetyl derivative melting at 249°, prepared by the action of acetic anhydride on the amine. When the base was refluxed for an hour with an excess of anhydride, with or without fused sodium acetate, we obtained a product melting at 248°, which was only exceptionally pure di-iodonitro-aniline.

Anal. (Carius). Calcd. for $C_8H_4O_2N_2I_2$: I, 65.11. Found: 64.97.

When 10 g. of the base was warmed with 35 cc. of anhydride containing five drops of concd. sulfuric acid, the *N*-diacetyl derivative melting at 169°¹⁰ was formed.

Anal. (Carius). Calcd. for $C_{10}H_8O_4N_2I_2$: I, 53.55. Found: 53.40, 53.45.

2-Bromo-4-nitro-aniline.—This substance has been made by a number of indirect methods.¹¹ The direct bromination has been stated⁹ to give a mixture difficult to separate, of mono- and dibromo derivatives. The following procedure was found effective. Seventy-five g. of *p*-nitro-aniline was dissolved by heating in 1000 cc. of concd. hydrochloric acid and the solution rapidly cooled to room temperature. The aspiration through the solution of 87 g. of bromine was begun promptly and completed during two hours with frequent agitation. The solution was then filtered and the solid agitated with a liter of water to hydrolyze the hydrochloride. The insoluble base was crystallized from 600 cc. of 65% alcohol. The yield, including two crops after concentration of the solution, was 81%; m. p., 104.5°. When the bromine was dissolved in concd. hydrochloric acid and added in this form, the yield was reduced and some of the dibromo derivative was formed.

2-Bromo-4-nitro-acetanilide.—Attempts to brominate *p*-nitro-acetanilide in acetic acid solution were not successful even when iron wire was added as catalyst. Acetylation of bromonitro aniline is moderately difficult. Chattaway and Orton¹² heated it with acetyl chloride at 130° and obtained a mono-acetyl derivative melting at 129°, but Körner and Contardi⁹ speak of an acetyl derivative (m. p., 114°) and a diacetyl derivative (m. p., 132°). To a mixture of 10 g. of bromonitro-aniline and 5 cc. of glacial acetic acid containing 5 drops of concd. sulfuric acid, was added 5 cc. of acetic anhydride and the whole was warmed until the yellow color disappeared. The nearly white product (10.5 g.) melted at 129–130°. It was also obtained when the base was boiled for an hour with acetic anhydride alone. Analysis showed it to be the mono-acetyl derivative.

2-Bromo-*p*-phenylenediamine.—The bromonitro-aniline was reduced as already described for the iodo compound, and the base extracted with ether. The product (yield, 75%) crystallized from carbon tetrachloride in white needles; m. p., 76°.

Anal. (Carius). Calcd. for $C_6H_7N_2Br$: Br, 42.73. Found: 42.86, 42.95.

2,5-Diacetylaminobromobenzene.—The acetylation offered no difficulty. The product melted at 200°.

Anal. (Carius). Calcd. for $C_{10}H_{11}O_2N_2Br$: Br, 29.48. Found: 29.61.

2-Bromo-4-amino-acetanilide.—Bromonitro-acetanilide was suspended in twice its weight of concd. hydrochloric acid and treated with 3 moles of $SnCl_2 \cdot 2H_2O$ in the same solvent. The mixture, which became somewhat warm, was stirred for half an hour, cooled and made alkaline with 50% sodium hydroxide solution. The gummy mass which separated gave crystals from benzene; m. p., 123°.

⁹ Körner and Contardi, *Atti accad. Lincei*, 22 [I], 825 (1913); *C. A.*, 8, 73 (1914).

¹⁰ Körner and Contardi (Ref. 9) give 171°.

¹¹ Hübner, *Ber.*, 10, 1709 (1877); *Jahresber.*, 305, 350, 1875, Ref. 9.

¹² Chattaway and Orton, *Ber.*, 33, 2398 (1900).

Anal. (Carius). Calcd. for $C_8H_9ON_2Br$: Br, 34.89. Found: 35.26, 35.36.

2,3,5-Tribromo-4-amino-acetanilide.—When 2.6 g. (2 molecular proportions) of bromine was aspirated into a solution of 2 g. of 3-bromo-4-amino-acetanilide in 50 cc. of glacial acetic acid, a solid tribromo derivative separated. After being treated with alkali to remove hydrobromic acid and crystallized from alcohol, it formed white needles; m. p., 207°. Smaller amounts of bromine gave the same product but in smaller yields.

Anal. (Carius). Calcd. for $C_8H_7O_2N_2Br_3$: Br, 61.97. Found: 61.99, 61.86.

The structure assigned is the one that would be expected from the method of preparation. By diazotization and reduction, the amino group was replaced by hydrogen. Hydrolysis of the product gave a substance melting somewhat indefinitely from 88 to 90°. The expected product, 2,3,5-tribromo-aniline, melts at 91°.¹³

Summary

1. Some new bromo and iodo derivatives of *p*-phenylenediamine have been described.

2. Determinations of the rate of halogen removal from *o*-iodo-aniline and from iodo- and bromo-*p*-phenylenediamine, under conditions designed to measure the positivity of the halogen in question, gave results in the ratio 69.0:6.9:2.6. These fall in the order predicted by the theory advanced.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

POSITIVE HALOGENS ATTACHED TO CARBON IN THE AROMATIC SERIES. IV. SELECTIVITY OF HALOGEN REMOVAL

BY BEN H. NICOLET AND REUBEN B. SANDIN¹

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In previous papers of this series² attention has been called to the tendency of bromine or iodine occupying certain specific positions in aromatic compounds to be removed by hydrolysis and replaced by hydrogen. Such halogens are to be found primarily in positions *ortho* or *para* to amino or hydroxyl groups, and their whole behavior is conveniently summed up in the statement that they react as somewhat positive halogens.

In studying the removal of such halogens it has often proved more convenient to perform the hydrolysis in the presence of stannous chloride in order to obviate effects due to resubstitution and to oxidation. It is believed that the presence of this reducing agent does not affect in any important way the primary reaction of halogen removal.^{2b}

¹³ Claus and Wallbaum, *J. prakt. Chem.*, [2] 56, 60 (1897).

¹ The material here presented was used by Reuben B. Sandin in partial satisfaction of the requirements for the degree of Doctor of Philosophy at the University of Chicago, 1924.

² (a) Nicolet, *THIS JOURNAL*, 43, 2081 (1921). (b) Nicolet and Sampey, *ibid.*, 49, 1796 (1927). (c) Nicolet and Ray, *ibid.*, 49, 1801 (1927).

The explanation advanced for the behavior of these reactive halogens implies that halogens in other positions in the molecule should show very different behavior and there is a large amount of evidence in the chemical literature to show that this is, at least qualitatively, the case. In the present paper, striking evidence of a more quantitative nature is presented.

3-Iodo-4-aminotoluene readily shows the reactions of positive iodine.^{2a,3} 2-Iodo-4-aminotoluene should not and, we find, does not show such reactions. A number of new derivatives of the latter substance, containing bromine or iodine in the 3 or 5 position, have been prepared and their hydrolysis with hydrochloric acid in the presence of stannous chloride has been studied. The results (Table I) indicate that under conditions which cause removal of iodine, or even of bromine, from the 3 or 5 position (with reference to methyl), the 2-iodine is completely unaffected. These results are fully in accord with the original assumptions and are considered, incidentally, as a further justification for the use of stannous chloride in this and earlier work.

A quantitative comparison of the rates of removal of iodine (Table II) from 2-iodo-aniline and from 2,5-di-iodo-4-aminotoluene (only the 5-iodine is removed in the latter case) has been made and the former reaction is found to be about one-third more rapid. Fair constants for the velocity of the reaction have been calculated on the assumption that it is not influenced by changes in the concentration of stannous chloride. The latter, however, is relatively large in these cases. More decisive results on this point⁴ have been obtained in other instances.

Experimental Part

2-Iodo-4-nitrotoluene.—*o*-Toluidine was nitrated by a method⁵ recommended for the nitration of *p*-toluidine; a 70% yield of crude 2-amino-4-nitrotoluene was obtained. The 2-iodo-4-nitrotoluene was made according to Willgerodt and Kok⁶ with a 90% yield. It formed nearly white crystals; m. p., 54°.⁷

2-Iodo-4-aminotoluene.—The nitro compound was reduced with tin and hydrochloric acid and the base recovered by steam distillation; yield, 90%. The pure substance melted at 39° and its acetyl derivative at 130°.⁸

2,5-Di-iodo-4-aminotoluene.⁹—A mixture of 5 g. of 2-iodo-4-aminotoluene, 5.4 g. of iodine, 2.5 g. of calcium carbonate and 10 cc. each of water and ether was refluxed on

³ Wheeler and Liddle, *Am. Chem. J.*, **42**, 453 (1909).

⁴ To be presented later by Dr. J. R. Sampey.

⁵ Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1924, vol. 4, p. 139.

⁶ Willgerodt and Kok, *Ber.*, **41**, 2077 (1908).

⁷ The melting point has previously been given as 58° (Ref. 6) and 51° [Reverdin, *Ber.*, **30**, 3000 (1897)].

⁸ Willgerodt and Gartner [*Ber.*, **41**, 2813 (1908)] reduced the nitro compound with ferrous sulfate and ammonia; their base melted at 37°; acetyl derivative, m. p., 130°.

⁹ Wheeler, *Am. Chem. J.*, **44**, 501 (1910).

a water-bath for three hours and then made alkaline and subjected to steam distillation. The 2,5-di-iodo derivative came over slowly and separated for the most part in the condenser. It formed needles from alcohol; m. p., 110°.

Anal. (Carius). Calcd. for $C_7H_7NI_2$: I, 70.75. Found: 71.0, 71.2.

One g. of the substance was heated to boiling under reflux for two hours with 10% hydrochloric acid. 2-Iodo-4-aminotoluene was the chief product. Iodine equivalent to 0.3 atom was deposited in the condenser; that in the solution was not determined.

2,5-Di-iodo-4-acetotoluide.—When the base was warmed with acetic anhydride the acetyl derivative was obtained. It formed white needles; m. p., 193°.

Anal. (Carius). Calcd. for $C_9H_9ONI_2$: I, 63.34. Found: 63.37, 63.47.

2-Iodo-5-bromo-4-acetotoluide.—2-Iodo-acetotoluide was dissolved in five parts of glacial acetic acid, treated with one mole of bromine and allowed to stand for 12 hours. The yield was nearly quantitative. The purified product formed white needles; m. p., 165–166°. When treated with additional bromine under similar conditions it did not react further.

Anal. (Carius). Calcd. for C_9H_9ONBrI : AgBr + AgI, 119.4. Found: 118.6, 118.4.

2-Iodo-5-bromo-4-aminotoluene.—The acetyl derivative was refluxed for ten minutes with 20% hydrochloric acid and the base was recovered by steam distillation; m. p., 86–87°.

Anal. (Carius). Calcd. for C_7H_7NBrI : AgBr + AgI, 135.0. Found: 135.7, 135.6.

2-Iodo-3,5-dibromo-4-aminotoluene.—2-Iodo-4-aminotoluene was brominated in glacial acetic acid solution, using two moles of bromine. The use of less bromine leads to the same product, mixed with unaltered material. After steam distillation, the substance crystallized from alcohol in light brown needles; m. p., 109°; yield, 75%.

Anal. (Carius). Calcd. for $C_7H_6NBr_2I$: AgBr + AgI, 164.6. Found: 164.0.

2-Iodo-3,5-dibromo-4-acetotoluide.—As might have been expected, the base did not acetylate readily. Acetic anhydride was without action but heating with acetyl chloride readily gave the acetyl derivative. From alcohol it separated in fine, white needles; m. p., 228–229°.

Anal. (Carius). Calcd. for $C_9H_6ONBr_2I$: AgBr + AgI, 141.0. Found: 140.3, 139.7.

2,3,5-Tri-iodo-4-aminotoluene.—To a solution of 5 g. of 2-iodo-4-aminotoluene in 50 cc. of glacial acetic acid was added 7.8 g. (2 moles) of iodine monochloride, and the mixture allowed to stand for 24 hours. A tarry mass separated. Water was added and the supernatant liquid decanted. On addition of alkali and steam distillation only 2,5-di-iodo-4-aminotoluene came over. When this was removed, the residue was extracted with hot alcohol and the solution decolorized with charcoal. Repeated recrystallizations from a mixture of alcohol and chloroform gave a small yield of light brown needles, melting constantly at 120–121°.

Anal. (Carius). Calcd. for $C_7H_6NI_3$: I, 78.55. Found: 78.42, 78.23.

The base was not acetylated by hot acetic anhydride. As acetyl chloride would probably have caused liberation of iodine, no further attempt at acetylation was made.

Action of Bromine on 2,5-Di-iodo-4-aminotoluene.—The di-iodotoluidine (0.5 g.) was dissolved in 15 cc. of glacial acetic acid. To this was added 0.44 g. (2 molecular proportions) of bromine, also dissolved in acetic acid, and the whole was allowed to stand for 24 hours. Addition of an excess of alkali and steam distillation gave 0.4 g. of a product melting at 108° which, when mixed with pure 2-iodo-3,5-dibromo-4-

aminotoluene, melted at 109° . The more mobile iodine had thus been replaced by bromine while the iodine in the 2 position was unaffected.

Hydrolysis and Reduction with Hydrochloric Acid and Stannous Chloride.—As some of the halogenated toluidines described above were difficultly soluble in hot hydrochloric acid, they were dissolved in a mixture of equal volumes of concd. hydrochloric acid and glacial acetic acid. The amount of amine was so chosen that the solution was approximately 0.055 *M* in each case. An excess of stannous chloride (2 moles for each atom of halogen present) was then added and the solutions were heated under reflux to active boiling for the times indicated in Table I.

In the last column of Table I are listed the products isolated in each case. These were identified by the melting points of the free base or acetyl derivative or both. In each instance the identification was confirmed by determining the melting point of a mixture of the product with a known sample of the pure substance. Large samples were not used and the difference between the reported totals and 100% represents losses in recovery and separation, rather than side reactions. In no case was there any indication of the removal of iodine in the 2 position with formation of *p*-toluidine.

TABLE I
REACTION WITH HYDROCHLORIC ACID AND STANNOUS CHLORIDE

Substance used	Time of hydrolysis, hours	Products recovered
2-Iodo-4-aminotoluene	8.0	Unaltered material only
2,5-Di-iodo-4-aminotoluene	0.5	20% unaltered; 30% of 2-iodo-4-aminotoluene
2,3,5-Tri-iodo-4-aminotoluene	1.5	No unaltered material; 50% of 2-iodo-4-aminotoluene
	1.5	2-Iodo-4-aminotoluene only
2-Iodo-5-bromo-4-aminotoluene	8.0	5% unaltered; 70% of 2-iodo-4-aminotoluene
2-Iodo-3,5-dibromo-4-aminotoluene	4.0	50% of 2-iodo-5-bromo-4-aminotoluene
	8.0	Chiefly 2-iodo-4-aminotoluene; a little 2-iodo-5-bromo derivative.

Quantitative Comparison of the Rates of Removal of Iodine from 2,5-Di-iodo-4-aminotoluene and 2-Iodo-aniline.—To a solution of 0.00066 mole of substance in 10 cc. of glacial acetic acid was added 5 cc. of 10% hydrochloric acid containing 0.5 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. In each experiment such a mixture was heated in a rapidly boiling water-bath for the time indicated, then quickly cooled and diluted with water. An extraction with chloroform at this point removed a small amount of material which otherwise gave an interfering color in the subsequent titration. Iodine was determined^{2b} by the method of Fresenius. The atomic % of iodine removed in each case, together with the values of *K* calculated

on the assumption that the reaction is of the first order, are given in Table II.

TABLE II
RATE OF IODINE REMOVAL

Time, min.	2-Iodo-aniline		2,5-Di-iodo-4-aminotoluene ^a	
	Reaction, %	K	Reaction, %	K
5	7.82	0.0165	6.72	0.0137
15	25.18	.0194	23.13	.0169
30	49.18	.0226	36.22	.0150
60	75.19	.0232	61.46	.0161
120	93.23	.0225	83.50	.0150

^a Only one iodine is reactive.

Summary

1. A number of new halogen derivatives of 2-iodo-4-aminotoluene have been prepared.

2. A study of the selectivity and rate of halogen removal in these compounds offers striking confirmation of predictions based on a consideration of the removable halogens as positive.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

POSITIVE HALOGENS ATTACHED TO CARBON IN THE AROMATIC SERIES. V. ANALOGY BETWEEN POSITIVE AND NEGATIVE HALOGENS

BY BEN H. NICOLET

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The pronounced reactivity toward all alkaline reagents of the halogens in 2,4- and 2,6-dinitrophenyl halides is well known. The halogens are removed as halide ion and replaced by —OH, —NH₂, etc. Very few chemists have hesitated to attribute this increase in reactivity to an increase in the negative character of the halogen in question by the nitro groups, which in turn are usually conceded, in recent years at least,¹ to be positive in character. The fact that no case was known in which a halogen attached to carbon in a benzene ring was given a conspicuously negative character by substituents occupying only positions *meta* to it, appears to have caused little apprehension.

Recent papers² from this Laboratory have discussed as positive certain halogens (bromine and, more conspicuously, iodine) which, when occupying positions *ortho* or *para* to one or more amino or hydroxyl groups, were

¹ Fry, "Electronic Conception of Valence," Longmans, Green and Co., 1921, p. 122. Stieglitz, *THIS JOURNAL*, **44**, 1305 (1922). Shoesmith, Hetherington and Slater, *J. Chem. Soc.*, 125, 1314 (1924).

² (a) Nicolet, *THIS JOURNAL*, **43**, 2081 (1921). (b) Nicolet and Sampey, *ibid.*, **49**, 1796 (1927). (c) Nicolet and Ray, *ibid.*, **49**, 1801 (1927). (d) Nicolet and Sandin, *ibid.*, **49**, 1806 (1927).

hydrolyzed (usually in acid solution) in such a way that the halogen was replaced by hydrogen, while the solution acquired oxidizing properties, as shown by the liberation of halogen, the formation of more highly substituted products, or the oxidation of suitable³ reducing agents. This interpretation appears to have been less widely accepted, perhaps because of its relative novelty, although reactions seeming to justify it have been found in all the suitable cases investigated.

The present paper records an unsuccessful attempt to demonstrate positive halogen in what is perhaps the ideal case of those subject to the limitation that only *meta* substituents should be present. 3,5-Dinitroiodobenzene has been prepared, and shown to have no appreciable tendency to split off iodine when heated at 100° in acid solution.

In this connection, however, it was decided to test also the ease of hydrolysis of 3,5-diaminochlorobenzene by alkalies. This compound contains its chlorine (the most negative of the halogens, with the exception of fluorine) *meta* to two amino groups. It was boiled for two hours with an alcoholic solution of sodium ethylate, and allowed to stand two days longer, without the slightest observable liberation of chloride ion. One is thus faced with the following paradox: two amino groups, suitably located, suffice to give to iodine (or even to bromine)⁴ a pronounced positive character; two nitro groups, suitably located, give to chlorine (or even to bromine or iodine) a pronounced negative character; but neither two nitro groups, both *meta* to halogen (even iodine), nor two amino groups, both *meta* to halogen (even chlorine) suffice to give a character which is definitely positive or negative, respectively.

One conclusion appears to be that the negativity and positivity, respectively, of halogens attached to carbon in the benzene ring, rest on approximately the same basis. A further conclusion might well be that if one is to assume polarity at all (and this seems necessary, to explain the great difference in character of the two types of reaction discussed), one must further assume that the character of the reaction is such that the latter is definitely conditioned by the presence of suitable groups in the *ortho* or *para* positions. The logical interpretation of this assumption would be that the reactions in each case are due to the possibility of the formation of intermediate products of a special (presumably quinoidal) type. A possible interpretation of this sort for the reactions of compounds assumed to contain positive halogens will be given below.

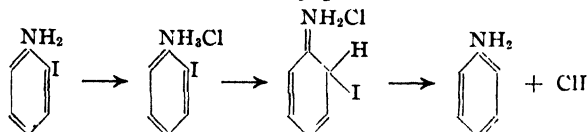
Extension of the reasoning outlined leads to another consequence. For those chemists who wish to attribute polar structures (or structures at least partially polar) to organic compounds in general, it may be nec-

³ Usually stannous chloride; as to its "suitability," see Ref. 2.

⁴ But not to chlorine which, however, shows similar properties in 2,4,6-triaminobenzene.

essary to recognize as a fact that non-reactivity, under given conditions, of a certain atom or radical has no bearing whatever on the structure to be attributed; or, to state it differently, altogether aside from the polar (or partially polar) structure which a given molecule may possess, demonstration of the structure in question by a given diagnostic reaction depends also on other conditions, which may or may not permit the expected reaction to take place.

The considerations discussed above suggest most strongly that both the types of hydrolysis mentioned take place through the formation of a quinoidal intermediate. In view of the discussions given by Robinson⁵ of 1,3 addition to α,β -unsaturated amino compounds, as a case of addition to a special type of conjugated system, it seems especially tempting to assume that the elimination of halogens in the positive form from amino derivatives⁶ of the type discussed, may take place by 1,3 elimination from an analogous system in the way pictured below.



It is an experimental fact that halogen is liberated in positive form when compounds of the type indicated are heated in acid solution. It is also an experimental fact, although the data have not yet been published, that in analogous cases a quantitative study of the reaction involved when analogous compounds are heated with acid and stannous chloride has shown that the reaction rate is not proportional to the concentration of the stannous chloride. It would seem to follow that the reaction in the presence of stannous chloride (which is the one more generally studied) is really a succession of reactions of which the first is simply one of hydrolysis (or at least one independent of the presence of the reducing agent), followed by the reduction of the positive halogen as it appears in the initial reaction. The mechanism may prove, on further study, to be other than that outlined above, but it is not believed likely that the principles stated will require serious modification.

Experimental Part

3,5-Diaminochlorobenzene.—This substance has been made by Cohn,⁷ by the reduction of 3,5-dinitrochlorobenzene. A method analogous to that by which Jackson and Calvert⁸ obtained the corresponding bromo compound was preferred.

⁵ (a) Hamilton and Robinson, *J. Chem. Soc.*, **109**, 1029 (1916). (b) Robinson, *ibid.*, **109**, 1038 (1916).

⁶ The possible extension of this type of reaction to phenolic derivatives is obvious.

⁷ Cohn, *Monatsh.*, **22**, 119 (1901).

⁸ Jackson and Calvert, *Am. Chem. J.*, **18**, 487 (1896).

2,4,6-Tribromo-3,5-dinitrochlorobenzene⁹ was reduced with tin and concd. hydrochloric acid; with the addition of some glacial acetic acid to increase the solubility of the dinitro compound, the reduction was completed in two hours on the water-bath. The product was further identified by the preparation of its diacetyl and dibenzoyl derivatives.⁷

ATTEMPTED HYDROLYSIS.—Jackson and Calvert⁸ say of 3,5-diaminobromobenzene, "Sodic hydrate seems to have no action even when warmed with it several minutes on the water-bath." One g. of 3,5-diacetylaminochlorobenzene was added to a solution of 2 g. of sodium in 50 cc. of alcohol; the mixture was refluxed for two hours, and allowed to stand for two days. The solution contained only a trace of chloride ion, and a control showed an equal trace in the sodium ethylate so prepared. It was shown that the acetyl derivative was completely hydrolyzed under the conditions present; on reacylation, more than 90% of the original material was recovered as the diacetyl derivative. There was thus no evidence of hydrolysis.

3,5-Dinitro-aniline.¹⁰—Flürscheim,¹¹ reviewing the work of Bader¹² and de Kock,¹³ described a method for obtaining this substance in 62% yield. A 74% yield was obtained as follows.

Hydrogen sulfide was passed into a mixture of 100 cc. of 95% alcohol and 60 cc. of concd. ammonium hydroxide until the weight increased 5.5 g. This solution was added drop by drop to a refluxing solution of 6 g. of 1,3,5-trinitrobenzene in 150 cc. of alcohol, and heating continued for one hour after addition was complete. The mixture was then collected, filtered to remove sulfur, and the alcohol distilled off. The residue was extracted thoroughly with hot water, and the extract concentrated till crystallization began, and then cooled in ice water. The product, recrystallized from hot water, melted at 155–156°.

3,5-Dinitro-iodobenzene.—The amino group was replaced by iodine in the usual way, and the product recrystallized from 60% alcohol. It formed golden plates; m. p., 99°.

Anal. (Carius). Calcd. for $C_6H_4O_2N_2I$: I, 43.26. Found: 43.14.

ATTEMPTED HYDROLYSIS.—Dinitro-iodobenzene (0.2 g.) was dissolved in 15 cc. of acetic acid and 15 cc. of 10% sulfuric acid added, and the mixture refluxed for one hour. No iodine color appeared, and the solution gave no test for inorganic iodine. Most of the material was recovered unaltered.

3,5-Diacetylamino-iodobenzene.—The dinitro-compound was reduced with tin and hydrochloric acid, and the tin removed with hydrogen sulfide. Excess of sodium acetate was added, and then an excess of acetic anhydride. The acetyl derivative which separated melted after recrystallization at 291°.

Anal. (Carius). Calcd. for $C_{10}H_{11}O_2N_2I$: I, 39.94. Found: 40.22.

Summary

1. 2,4-Dinitrochlorobenzene and 2,4-diamino-iodobenzene are known to behave on hydrolysis as though their halogens were negative and positive, respectively. 3,5-Diaminochlorobenzene and 3,5-dinitro-iodo-

⁹ Jackson and Carlton, *Am. Chem. J.*, **31**, 375 (1904).

¹⁰ The remainder of the experimental work described was carried out by Mr. Ben Wilbur Goldman.

¹¹ Flürscheim, *J. prakt. Chem.*, [2] **71**, 537 (1905).

¹² Bader, *Ber.*, **24**, 1655 (1891).

¹³ de Kock, *Rec. trav. chim.*, **20**, 112 (1900)

benzene (both ideal cases, in terms of the theory discussed) have been prepared, and show no indications of polar characteristics for the halogens present.

2. A possible mechanism for the elimination of positive halogen from amino derivatives, involving the formation of a quinoidal intermediate compound and subsequent 1,3 elimination, has been suggested.

3. It is pointed out that failure to react under given conditions is no adequate indication of polar structure.

4. The assumption of negativity and positivity, respectively, for certain halogens attached to carbon in the benzene ring, is shown to rest on essentially the same basis.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY, No. 303]

ADDITION COMPOUNDS OF ALLYLTHIO-UREA WITH SILVER HALIDES¹

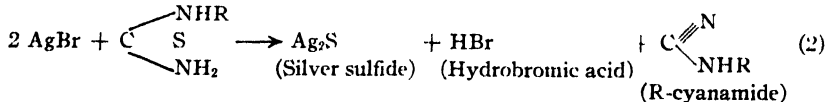
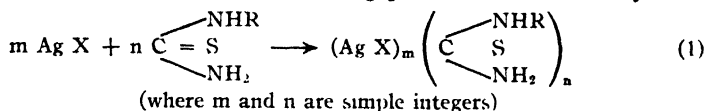
BY S. E. SHEPPARD AND H. HUDSON

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In an investigation on photographic gelatin² it was found that the photographic activity of certain gelatins depends upon the presence of traces of mustard oil, or allyl isothiocyanate, and the thio-urea (allyl thiocarbamide, thiosinamine) derived therefrom. Further, it was shown that this photographic sensitizing power was a general property of thio-ureas and a number of cognate bodies,² being due to the formation of small traces of silver sulfide in the silver halide grains. These traces of silver sulfide were considered to constitute the so-called "sensitivity centers" of photographic theory.

The chemical reactions in this sensitizing process are essentially



In Reaction 2 sufficient alkalinity is necessary to neutralize the hydrobromic acid and the cyanamide.

The present investigation is concerned with the formation and properties of the intermediate double compounds of silver halide and thio-

¹ Read in part at the Regional Meeting of the American Chemical Society, January, 1926.

² Sheppard, *Phot. J.*, **65**, 380 (1925).

urea, indicated in Reaction 1. So far not very much information has been found in the literature concerning such compounds. Reynolds³ described a definite crystalline compound of silver bromide with thio-urea, $(\text{CSN}_2\text{H}_4)_2 \cdot \text{AgBr}$, obtained by the interaction of silver nitrate with $(\text{CSN}_2\text{H}_5)_4\text{NBr}$ in equimolecular proportions. He further stated that analogous compounds had been obtained with other silver salts, and later described these.⁴ With silver nitrate, the general result was the identification of the compounds $(\text{CSN}_2\text{H}_4)_3 \cdot \text{AgNO}_3$ and $(\text{CSN}_2\text{H}_4) \cdot \text{AgNO}_3$, while some evidence of the existence of the intermediate substance, $(\text{CSN}_2\text{H}_4)_2 \cdot \text{AgNO}_3$, was obtained.

Coming to the silver halides, he found that *silver bromide* forms two compounds with thio-urea, $(\text{CSN}_2\text{H}_4)_2 \cdot \text{AgBr}$ and $\text{CSN}_2\text{H}_4 \cdot \text{AgBr}$. With *silver chloride* he obtained only the 2:1 compound, with no evidence for the 1:1 compound, and with *silver iodide* only the 1:1 compound. It may be noted that while Reynolds obtained only a 2:1 compound with silver cyanide, and states that "as with silver chloride, a 1:1 compound has not been obtained," Rosenheim and Loewenstamm⁵ obtained by digestion of freshly precipitated silver cyanide in aqueous thio-urea white, glistening scales of a 1:1 compound, which they describe as "extraordinarily unstable, separating silver sulfide again on recrystallization."

When we turn to the substituted thio-ureas, the previous indications are much more meager. We have not yet had access to a dissertation by Falke⁶ which contains some previous work on compounds of the metal salts with thiosinamine (allyl thiocarbamide). In this a 1:1 compound with silver chloride is mentioned, occurring in "white, feathery needles."

Silver Chloride and Thiosinamine.—The compound was prepared by mixing equimolecular quantities of allyl thiocarbamide, potassium chloride and silver nitrate, each at 0.1 *M* concentration. A microcrystalline precipitate is at once formed which was filtered off and washed free from soluble salts. Analysis of this gave sulfur and silver chloride corresponding to the 1:1 compound, $\text{NH}_2 \cdot \text{C}(-\text{S})\text{NHC}_3\text{H}_5 \cdot \text{AgCl}$. Solubility measurements were made on this by percolating the powder with

TABLE I
SOLUBILITY OF $\text{NH}_2 \cdot \text{CS} \cdot \text{NHC}_3\text{H}_5 \cdot \text{AgCl}$

Temp., °C.	Subs. per liter, g.	Subs. per liter, g. moles $\times 10^4$
15	0.0517	2.0
25	.0816	3.1
35	.1313	5.0
50	.4578	17.6

³ Reynolds, *J. Chem. Soc.*, **53**, 857 (1888).

⁴ Reynolds, *ibid.*, **61**, 249 (1892).

⁵ Rosenheim and Loewenstamm, *Z. anorg. Chem.*, **34**, 62 (1903).

⁶ Falke, Dissertation, Marburg, 1893 *Beilstein*, **4**, 210 (1922).

distilled water at various temperatures, until saturation values were reached on analysis of the supernatant liquid.

Silver Bromide and Thiosinamine.—For the preparation of the 1:1 compound, a quantity of well-washed silver bromide was fused in a porcelain crucible. Two glass rods were allowed to freeze in the melt, and served as supports after the crucible was broken away. The fused mass was cleaned by immersion in sodium thiosulfate solution and water, and then suspended in an aqueous solution of allyl thiocarbamide (thiosinamine), one part in 1000 parts of water. Bunches of small, needle-shaped crystals developed on the surface of the silver bromide overnight (Fig. 1). A quantity of crystals were grown in this manner, washed with distilled water and dried over sulfuric acid. Analysis was made of the silver content by digestion with ammonium sulfide, the silver sulfide formed being filtered off, dried and weighed. A sample analysis follows.



Fig. 1 Crystals of allyl thiocarbamide—silver bromide. Magnification eight times.

Anal. Subs., 0.1534 Ag_2S calcd. for $\text{AgBr} \cdot \text{C}_4\text{N}_2\text{H}_5\text{S}$, 0.0626. Ag : calcd., 35.50. Found: 35.51.

Control analyses of the nitrogen by Kjeldahl's method confirmed this, corresponding to 97.4% of that calculated for $\text{AgBr} \cdot \text{C}_4\text{N}_2\text{H}_5\text{S}$. This compound corresponds, therefore, to the 1:1 compound of silver bromide and thio-urea, described by Reynolds, and the 1:1 compound of silver chloride and thiosinamine, ascribed to Falke.

Solubility measurements were made on the 1:1 silver bromide compound at 15, 25, 35 and 50°. A quantity of the compound was put in known volumes of water and shaken for 48 hours in a thermostat kept constant to 0.1°, and the amount dissolved determined by conversion to silver sulfide. The values obtained are given in Table II.

TABLE II
SOLUBILITY OF $\text{C}_4\text{N}_2\text{H}_5\text{S} \cdot \text{AgBr}$

Temp., °C.	Subs. per liter, g.	Subs. per liter, g. moles $\times 10^4$
15.0	0.0446	1.46
25.0	.071	2.33
35.0	.120	3.94
50.0	.293	9.63

Silver Iodide and Thiosinamine.—Although there was evidently an action of dilute thiosinamine solution upon fused silver iodide, it was

not found possible to grow crystals in the same way as with silver bromide. An attempt to prepare the 1:1 compound was made as follows.

Eleven and six-tenths g. of allyl thiocarbamide and 16.6 g. of potassium iodide were dissolved in 500 cc. of water. To this there was slowly added with stirring 17.0 g. of silver nitrate in water. A voluminous precipitate formed which settled to the bottom, consolidating to a sticky, plastic mass. The supernatant liquor gave no reaction for silver sulfide when heated with ammonia. From this it appears that the 1:1 compound is formed, and that its solubility at room temperature is of the order of silver iodide or silver sulfide.

The solid decomposes very readily, giving silver sulfide, so that it appears that the following reaction had gone to completion: $\text{AgNO}_3 + \text{C}_4\text{N}_2\text{H}_8\text{S} + \text{KI} = \text{AgI} \cdot \text{C}_4\text{N}_2\text{H}_8\text{S} + \text{KNO}_3$. The compound was difficult to isolate in a pure state because it formed a glassy mass instead of crystallizing. It appears, however, somewhat soluble in alcohol from which it may be precipitated in a semi-colloidal state by the addition of water.

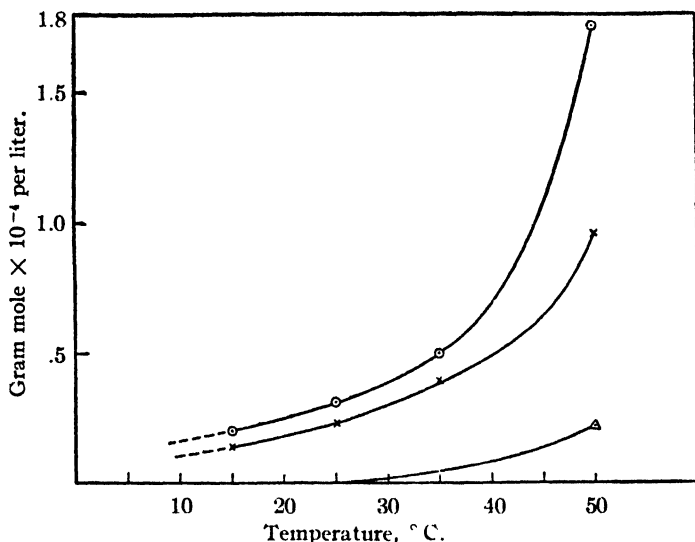


Fig. 2.—Solubility of silver halide-allyl thiocarbamide compound in water. \circ , silver chloride; \times , silver bromide; \triangle , silver iodide.

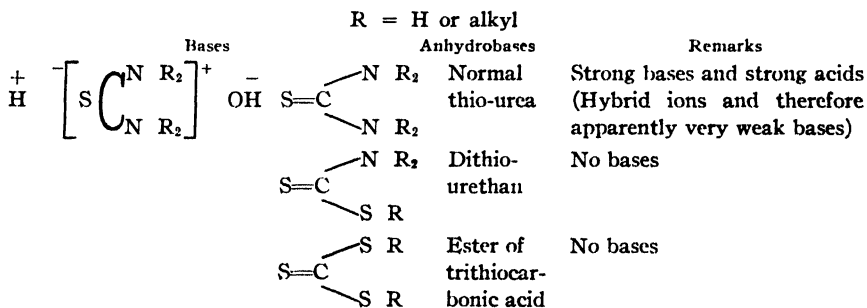
A solubility determination was made at 50° with the result given in Table III.

TABLE III		
Temp., $^\circ\text{C}$.	Subs. per liter, g.	Subs. per liter, g. moles
25		ca. 2.5×10^{-7}
50	0.0778	2.21×10^{-4}

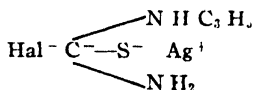
Effect of Soluble Halides.—Preliminary measurements have shown that excess of the soluble halides reduces the solubility of the double compounds in water. This effect is being studied, as well as the influence of excess of soluble halides and other salts on the formation of the double compounds and on their decomposition.

Composition and Constitution.—On comparing our observations with those of previous observers, we may note that although in several of our experiments considerable excess of allyl thiocarbamide was used over the 1:1 molecular ratio of silver halide:allyl thiocarbamide, and up to 1 mole of silver halide to 2 moles of allyl thiocarbamide, no evidence of other double compounds, for example, $1\text{Ag Br} : 2\text{C}_4\text{H}_8\text{N}_2\text{S}$, was obtained, but only of solutions. It is possible, therefore, that the 1:2 compound of allyl thiocarbamide is more difficult to isolate than that of thiocarbamide itself, and this is being investigated.

The compounds of thio-ureas with metal salts have been considered from the point of view of the Werner coordination theory by Rosenheim and Loewenstamm.⁵ The mode of combination of the silver halide will depend upon the constitution assigned to the thio-ureas. Lecher and co-workers⁷ in an important memoir on the "Constitution of Thiourea and the Thiourea Salts" give strong evidence for the ampholytic character of thio-urea, according to the following general scheme.



On this conception, the 1:1 double compounds would have the constitution



The contiguity of the silver ion and the negative sulfur atom agrees with the ready formation of silver sulfide.

Relation to Photographic Sensitizing.—The isolation and observed solubilities of these double compounds have important bearings on photographic sensitization, which will be discussed elsewhere. It may be suggested, however, that the much lower solubility of the silver iodide compound, compared with that of the 1:1 silver bromide compound, make it an important intermediate in the process.

It is known not only that silver iodide in small amounts (less than 3%) considerably influences photographic sensitivity, but also that in certain

⁷ Lecher and co-workers, *Ann.*, **445**, 35 (1925).

high-speed emulsions the proportion of iodide is greater in the larger than in the smaller grains.⁸ Further, it has been shown by Sheppard, Wightman and Trivelli⁹ and by Clark¹⁰ that the larger grains resist desensitizing more than the small ones. This may be due to the silver sulfide nuclei being larger or more firmly "rooted," and protected by silver iodide rather than silver bromide, in the larger grains.

Summary

1. The literature on the double compounds of thio-ureas with silver salts is briefly reviewed.
2. The preparation of the 1:1 compounds of allylthio-urea with silver chloride, silver bromide and silver iodide is described.
3. Solubility measurements are given for the temperature range 15 to 50°.
4. The constitution of these double compounds is discussed and their relation of photographic sensitizing.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

PHOTOSYNTHESIS WITH MALACHITE GREEN

BY DEAN BURK

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According to Baly, Heilbron and Barker¹ and Baly,² "an aqueous solution of malachite green saturated with carbon dioxide yields formaldehyde on exposure to light behind a thick plate glass screen. In the absence of carbon dioxide no formaldehyde is produced." No details of technique in support of this claim were offered. Baur and Büchi³ repeated the experiment, but they were unable to conclude that the formaldehyde came from the carbon dioxide. Indeed there was no doubt, from their experiments, that the presence of carbon dioxide in the exposed solutions of malachite green, the concentrations of which varied eight-fold, from 15 to 125 parts per million, reduced the yield of formaldehyde. When the absence of all carbonate or bicarbonate ions was insured by the addition of varying amounts of barium hydroxide, the yields of formaldehyde were increased decidedly, even though the solutions may have been partially or entirely discolored before exposure was made, owing to the alkalinity. The fact that the colorless solutions, when

¹ Renwick, Baldsiefen and Sease, *Phot. J.*, **66**, 163 (1926).

² Sheppard, Wightman and Trivelli, *Trans. Faraday Soc.*, **19**, 296 (1923).

¹⁰ Clark, *Phot. J.*, **64**, 91 (1924).

¹ Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1032 (1921).

² Baly, *Rec. trav. chim.*, **41**, 528 (1922).

³ Baur and Büchi, *Helv. Chim. Acta*, **6**, 959 (1923).

exposed, gave relatively large amounts of formaldehyde, combined with the fact that the yield was reduced when the insolation was made behind glass walls of increasing thickness, strongly supported the view that only the colorless ultraviolet rays were responsible for the photochemical effect, and still further weakened the original conception of Baly, Heilbron and Barker that carbon dioxide could be reduced by *visible* light when a photochemical catalyst like malachite green, which may combine with it, is present also. Baly has since reversed his position, and has stated⁴ that formaldehyde may form even in the absence of carbon dioxide. The present paper will offer evidence, obtained by experimental methods different from those previously used, which extends the general findings of these investigators.

Experimental Part

The new experimental feature of the technique was the use of condensed sunlight. The lenses were large, spherical, colorless, common glass flasks 30 cm. in diameter filled with clear water and mounted on stationary iron tripods. Calculations indicated that the intensity of sunlight which had passed through them was increased to a maximum of approximately 5000-fold; for noon sunlight this intensity would be about five million times that of an ordinary 40-watt Mazda lamp. Exposure behind one of these lenses on a clear day was considered to be equal, as regards the amount or total energy value of the light, to exposure to ordinary sunlight for about a month of clear days. (This assumption was confirmed experimentally by study of other relatively uncomplicated reactions, such as the reduction of Fehling's or Benedict's solutions, the decomposition of uranyl formate, etc., where justifiable interpretation was allowable because the rates of reaction were rapid enough and the equilibrium points far enough on the sides of the resultants.) The beam of light was generally 6 mm. in diameter at the point where it entered the exposed solution. The temperature of the solution was kept below 30° by immersion of the containing vessel a little below the surface of a simple water-bath. The solutions, whose concentrations in these experiments were always 50 parts per million (0.005%) of malachite green chloride, were exposed in glass bulbs blown on the end of common soft glass tubes about 30 cm. in length and 12 mm. in diameter. The bulbs were quite spherical, had a capacity of from 15 to 50 cc., were just as thin as safety would allow (from 0.05 to 0.1 mm.), and were very transparent. The tubes were cleaned with chromic acid at 100°, hot alcoholic potassium hydroxide, hot concd. nitric acid, and many rinsings of distilled water. (In order to allow for the movement of the sun, the positions of the bulbs were changed every 20 minutes. No heliostat was employed.) The tubes were exposed to lenses for four to six hours a day, but they also

⁴ Baly, *Ind. Eng. Chem.*, **16**, 1016 (1924).

received the ordinary sunlight during the remaining hours. A control tube containing a solution of similar composition, but protected from light by being heavily wrapped in tin foil, was placed beside each exposed tube, in the same thermostat. Since the two corresponding tubes were treated as exactly alike as possible (except that their volumes frequently differed), except for exposure, any difference found between their contents upon examination could be considered as having been caused by either primary or secondary effects of light. The unexposed tubes were numbered "a." The sealed tubes were first evacuated with a water pump. The unsealed tubes were protected by hoods of tin foil bent over in such a manner as to allow entrance of air but to exclude foreign matter. The water used to make up the solutions was twice distilled and had a conductivity not greater than 5×10^{-6} mhos.

The ammonium carbonate used was Baker's $(\text{NH}_4)_2\text{CO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$, mol. wt. 174.15; 0.18 cc. of the 35.0 *N* sulfuric acid used in Expts. 9 and 10 was required to neutralize 0.500 g. of it to full methyl orange. The acid was contained in a side arm sealed into the neck of the tube, and was not mixed with the rest of the contents until after vacuum sealing. Ammonium carbonate was used since, if formaldehyde and oxygen gas were the photochemical end-products of the reaction to be studied, the ammonia could possibly assist in removing both of them, by forming hexamethylenetetramine (and other bases) as well as nitrites and nitrates.

Expts. 1-6 and 11-12 were exposed to lenses for 19 hours during December 27 to 30. Expts. 7-10 were exposed to lenses for 25 hours during December 15 to 23.

Results and Discussion

Table I contains the results of the experiments selected for mention.

The magnitudes of the concentrations of formaldehyde found agree exactly with those observed by Baur and Büchi.³ In acid solutions there was never more than 1 p.p.m. (part per million), generally much less; in the most alkaline solutions, 4 to 6 p.p.m. The Schryver test as employed by the writer was sensitive to 0.1 p.p.m., the Gallic acid test to exactly 1 p.p.m. This explains why in solutions where 1 p.p.m. or less was found by Schryver's, the Gallic test was negative. The standard solutions for comparison were made up in the presence as well as the absence of malachite green. At 1 p.p.m. of formaldehyde neither test is affected (within 10%) by the presence of 50 p.p.m. of malachite green, since the strong acidity of both sets of reagents instantly destroys the color of the dye. Baur and Büchi's statement that the presence of air makes little difference in the amount of formaldehyde formed is confirmed. Under the experimental conditions employed it would require a statistical study of many repeated experiments to show a real difference. The fact that the Gallic test, which is a good hydrolyzing agent on account

TABLE I
 0.005% MALACHITE GREEN

No.	Treat- ment	Color of solution	Vol., ^a cc.	pH	A ^b	B ^c	Schryver, p.p.m.	Gallic, p.p.m.	Nessler	
1	Unsealed	Intense blue-green	52	6.5	0.00	6	0.6-1	None	Slight ppt.	white
1a	Same, unexposed	Intense blue-green	41	6.5	.00	6	None	None	None	
2	Unsealed, + 1 drop of concd. NaOH	Colorless, cloudy (yellow tinge)	35	>10	.03	2	4 -6	4-6	Slight ppt.	white
2a	Same, unexposed	Colorless, cloudy	30	>10	.03	2	None	None	None	
3	Unsealed, + H ₂ SO ₄ to pH 2.0	Intense blue-green	25	2.0	.00	7	0.1-0.4	None	Very white ppt.	slight
3a	Same, unexposed	Intense blue-green	15	2.0	.00	7	None	None	None	
4	Sealed	Intense blue-green	30	6.5	.00	6	0.6-1	None	Slight ppt.	white
4a	Same, unexposed	Intense blue-green	18	6.5	.00	6	None	None	None	
5	Sealed, + 1 drop concd. NaOH	Colorless, cloudy (yellow tinge)	35	>10	.03	2	4 -6	4-6	Slight ppt.	white
5a	Same, unexposed	Colorless, cloudy	31	>10	.03	2	None	None	None	
6	Sealed, + H ₂ SO ₄ to pH 2.0	Intense blue-green	30	2.0	.00	7	Tr. ? (0.1-0.2?)	None	Very white ppt.	slight
6a	Same, unexposed	Intense blue-green	20	2.0	.00	7	None	None	None	
7	Unsealed, + 0.50 g. of (NH ₄) ₂ CO ₃	Colorless, cloudy	36	8.6	1.0	2	-4	2.4	Heavy yellow- red ppt.	
7a	Same, unexposed	Very light blue	48	8.3	1.0	2	None	None	Heavy yellow- red ppt.	
8	Sealed, + 0.50 g. of (NH ₄) ₂ CO ₃	Colorless, cloudy	32	8.6	1.1	1	-2	1-2	Heavy yellow- red ppt.	
8a	Same, unexposed	Very light blue	17	8.3	1.1	2	None	None	Heavy yellow- red ppt.	
9	Same as 8, + 0.12 cc. of H ₂ SO ₄	Intense blue-green	29	7.2	0.04		Tr. ? (0.1-0.2?)	None		
10	Same as 8, + 0.22 cc. of H ₂ SO ₄	Blue	34	2.0	0.4		Tr. ? (0.1-0.2?)	None		
11	Unsealed, + HCHO to 100 p.p.m.	Intense blue-green	35	6.5			100	100	Black-gray ppt.	
11a	Same, unexposed	Intense blue-green	26	6.5			100	100	Dark brown ppt.	
12	Sealed, + HCHO to 100 p.p.m.	Intense blue-green	24	6.5			100	100	Black-gray ppt.	
12a	Same, unexposed	Intense blue-green	14	6.5			100	100	Dark brown ppt.	

^a Of solution.^b A = cc. of 0.1 N acid or base required to neutralize 1 cc.^c B = drops of 0.005 N permanganate required by 1 cc.

of the practically pure sulfuric acid which it contains, never indicates a greater concentration than does the Schryver test is good inferential evidence that little or none of the formaldehyde is being removed by the formation of condensation compounds with malachite green or any of its photochemical decomposition products, such as amines. This might be expected, perhaps, since at this dilution the free energies of such reactions would be unfavorable to condensation. These experiments make it plain why Baur and Büchi found that carbon dioxide decreased the concentration of formaldehyde observed and that barium hydroxide

increased it; the amount is controlled by either the primary or secondary effects of the hydroxyl-ion concentration. The production of these small amounts of formaldehyde from malachite green was found by the writer to be practically independent, within ranges of 100-fold or more, of the intensity of the sunlight and the length of exposure (and the concentration of malachite green). Therefore, if solutions of from about 25 to 250 p.p.m. of malachite green were exposed to sunlight in the presence of carbonic acid (etc.) at a P_H less than 10, the finding of perhaps five or more p.p.m. of formaldehyde would be, contrary to current opinion and the opinion of the investigators cited,³ quite significant in relation to carbon dioxide reduction. In acid solutions, as little as 1 p.p.m. would be significant. This view is supported by the fact that while the maximum concentration of formaldehyde which could form from a solution of 50 p.p.m. of malachite green, on the basis of all its carbon molecules, is 44 p.p.m. (88.2%), nevertheless, if the benzene ring carbon molecules are not considered, but only the four methyl radicals, the maximum concentration would be only seven p.p.m. (15.1%). While it is probable that the significant amounts suggested above have not been found by any workers, it must be remembered that the experimental conditions have been quite simple, and others might be devised where the desired result would be obtained. It is conceivable that conditions could be obtained where the amount of formaldehyde formed from the dye would be entirely unqualifying, that is to say, a concentration less than 0.1 p.p.m.

The potassium permanganate titration values indicate no significant change as regards the formation of reducing substances such as hydroxylamine and formic acid, since each exposed solution had the same value as its corresponding unexposed one.

The Nessler tests show that bases, presumably amines, are formed upon exposure. The amount of photochemical nitrogen decomposition as amines was greater by several times than the amount of carbon decomposition as formaldehyde. The amounts of amines found are smaller in acid solutions. The reaction is shown to be entirely photochemical.

The values for P_H are accurate to 0.4, since the color of the dye interfered somewhat.

Expts. 7 to 10 show that the presence of ammonium, carbonate or bicarbonate ions, or of carbonic acid, have in no way affected the amount of formaldehyde formed, the P_H being taken into consideration.

The following results could not be placed conveniently in the table.

Griess, Trommsdorff and diphenylamine tests were negative in all cases except Expts. 2 and 7, where the presence of 1 p.p.m. of nitrite was indicated, showing that for the oxidation of the ammonia or other decomposition products of malachite green, conditions of exposure to sunlight, aeration and alkalinity are necessary. The Griess and Tromms-

dorff tests were sensitive to 0.1 p.p.m., the diphenylamine to about 1 p.p.m. At 1 p.p.m. of nitrite, smaller amounts of nitrate also present could not be distinguished. The usual method of reducing the nitrate with zinc and testing for increase of nitrite by the Griess test, which is specific, would not suffice. The amount of nitrite formed is not dependent on the ammonium-ion concentration, since Expt. 7 contained much more of the latter than did Expt. 2. The role of air is not known, but simple absorption of atmospheric oxygen-nitrogen compounds is precluded by experiments not reported in which many unexposed, unsealed tubes were found never to contain nitrites. While ammonia may be oxidized to nitrates and nitrites by short-wave ultraviolet light⁵ (200m μ), the oxidation of ammonia or ammonia-like forms, amines, etc., in the presence of sunlight-absorbing compounds, is not without example, as will be indicated in a later publication. The writer has found that ferric chloride, zinc oxide and mercuric oxide can oxidize ammonia to nitrites or nitrates in the presence of sunlight.

No odor was detected in any tubes, except that of ammonia in Expts. 7, 7a, 8 and 8a.

Reduction of Fehling's solution and the Molisch carbohydrate test were negative in all cases except, of course, in Expts. 11, 11a, 12 and 12a, where they were all of equal magnitude. No red ring was observed in the Molisch test, but rather the typical white cloud, insoluble in concd. sulfuric acid, given by formaldehyde.

All of the solutions except 2 and 2a gave the same slight black precipitate with iodine in potassium iodide solution (12.5 g. of iodine in a solution of 16.5 g. of potassium iodide in 100 cc. of water). When formaldehyde was added before the reagent (Thatcher test), all of the solutions gave the same kind and amount of precipitate except 2, 2a, 5, 5a, which gave smaller precipitates, and 11, 11a, 12, 12a, which gave also C₆H₁₂-N₄I₄, hexamethylenetetraminetetra-iodide.

The writer wishes to express his appreciation of assistance and advice offered by Professor Dennis R. Hoagland.

Summary

1. While previous observations have indicated that malachite green decomposes in sunlight to yield formaldehyde, the present experiments show that amines are produced also, and in greater concentration than formaldehyde. When the conditions are aerobic and alkaline, nitrites are produced also.

2. The interpretation of photosynthetic experiments with malachite green solutions is prejudiced little if any by the formation of formaldehyde

⁵ Berthelot and Gaudechon, *Compt. rend.*, **152**, 522 (1911). Baly, Heilbron and Stern, *J. Chem. Soc.*, **123**, 185 (1923).

from the dye itself, since the order of magnitude of the concentration of formaldehyde is extremely small, without exception, and can be controlled at will by varying the experimental conditions, particularly of hydrogen-ion concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN CINNAMYL CHLORIDE, MAGNESIUM AND CARBON DIOXIDE

BY HENRY GILMAN AND STANTON A. HARRIS

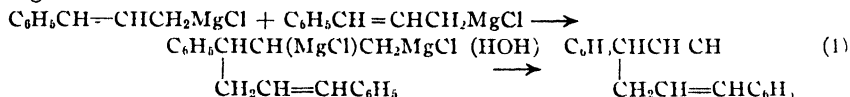
RECEIVED APRIL 16, 1927

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Introduction

In several quantitative studies, it has been proved that a few typical organomagnesium halides do not add to a wide variety of ethylenic and acetylenic hydrocarbons. Gilman and Crawford¹ used ethylmagnesium iodide with 11 ethylenic hydrocarbons; Gilman and Shumaker² used ethylmagnesium bromide and iodide with four acetylenic compounds; and Gilman and Peterson³ used ethylmagnesium bromide, phenylmagnesium bromide, butoxymagnesium iodide, *p*-tolylmercaptomagnesium iodide, methylaniline-magnesium bromide and ethylzinc iodide with 18 variously substituted ethylenic compounds.

A recent book⁴ and review⁵ of the chemistry of organomagnesium halides direct attention to the work of Rupe and Bürgin⁶ who have presumably proved that cinnamylmagnesium chloride (and bromide) adds to the ethylenic linkage of the cinnamyl group. They postulate the following reactions.



In support of the hydrocarbon (1,4-diphenyl-hexene-1) obtained by the addition of one molecule of cinnamylmagnesium chloride to the ethylenic linkage of another like molecule, they obtained phenylsuccinic and benzoic acids among the products of oxidation of their hydrocarbon. They were unsuccessful in their attempts to effect a reaction between the cinnamylmagnesium chloride (or bromide) and aldehydes or ketones.

The hydrocarbon which they obtained in limited amounts after eight

¹ Gilman and Crawford, *THIS JOURNAL*, **45**, 554 (1923).

² Gilman and Shumaker, *ibid.*, **47**, 514 (1925).

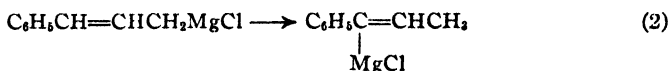
³ Gilman and Peterson, *ibid.*, **48**, 423 (1926).

⁴ Courtot, "Le Magnesium en Chimie organique," pp. 54, 318. Published by the author at Nancy, 1926.

⁵ Grignard, *Bull. soc. chim.*, **39**, 1285 (1926).

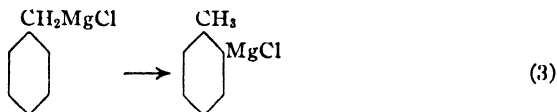
⁶ Rupe and Bürgin, *Ber.*, **43**, 172 (1910).

fractional distillations has not as yet been identified by us. However, their mechanism of reaction is probably incorrect. A Grignard reagent is formed when cinnamyl chloride reacts with magnesium in ether. This RMgX compound is not the cinnamylmagnesium chloride which they postulate in the explanation of the ethylenic hydrocarbon. Instead, it is an RMgX compound formed by the rearrangement of the cinnamylmagnesium chloride.



Evidence for the correctness of the RMgX compound formed by rearrangement is the production of methyl atropic acid, $\text{C}_6\text{H}_5\text{C}(=\text{CHCH}_3)\text{-COOH}$, when cinnamyl chloride and carbon dioxide are added to magnesium under ether.

Rearrangements of this type have previously been noted by others with related Grignard reagents. For example, benzylmagnesium chloride⁷ with formaldehyde gives *o*-tolylcarbinol and not β -phenylethyl alcohol. Here we have a comparable rearrangement, where the -MgCl group may be assumed to have gone from an alpha to a gamma carbon atom.



So far as known, carbon dioxide has not given such rearrangement reactions with benzylmagnesium chloride and triphenylmethylmagnesium chloride. The reagents that generally induce such rearrangement are formaldehyde and benzaldehyde. Some unpublished work with J. E. Kirby on the mechanism of these rearrangements shows that ethyl chlorocarbonate gives the *ortho* product of rearrangement with benzylmagnesium chloride (namely, ethyl *o*-toluate), and that α -naphthylmethylmagnesium chloride gives abnormal products with both formaldehyde and ethyl chlorocarbonate.

Experimental Part

The cinnamyl chloride was prepared in 78% yield according to Rupe and Bürgin.⁶ It was used in preference to the bromide, because such chlorides give a higher yield of RMgX compound than do the corresponding bromides.⁸ One-half of the magnesium they used was activated

⁷ Schmidlin and Garcia-Banús, *Ber.*, 45, 3193 (1912). In this article mention is also made of the rearrangement of triphenylmethylmagnesium chloride. References are given to the earlier work on both benzylmagnesium chloride and triphenylmethylmagnesium chloride.

⁸ Gilman and McCracken, *THIS JOURNAL*, 45, 2462 (1923). Gilman and Kirby, *ibid.*, 48, 1733 (1926).

according to the method of Baeyer.⁹ In our first experiments, the reaction was started with a very small amount of the highly active magnesium-copper alloy of Gilman, Peterson and Schulze.¹⁰ Later, however, it was found that the reaction started comparatively easily by the usual addition of a crystal of iodine, accompanied by moderate heating.

When allowed to proceed at room temperature, the reaction is quite vigorous and a positive color test for Grignard reagent was obtained by the use of Michler's ketone as described by Gilman and Schulze.¹¹ However, when the reaction mixture is heated prior to removing the small sample for a color test, no Grignard reagent is present. Accordingly, in subsequent runs, the reaction mixture was cooled moderately, and a stream of carbon dioxide was bubbled through the ether simultaneously with the addition of cinnamyl chloride. Because the reaction slowed down too decidedly when the cooling was effected by an ice-water bath, the cooling medium selected was running tap water.

Under these conditions, 3.7 g. or an 11.4% yield of an acid melting at 135–136° was obtained from 30.5 g. or 0.2 mole of cinnamyl chloride. In another 0.2-mole run the volume of ether was increased from 100 cc. to 500 cc., the reaction having been started with several cc. of cinnamyl chloride in 50 cc. of ether before bubbling in carbon dioxide at about 20°. The yield of acid from this run was 8.8 g., or 27.1%.

In this second run the acid was obtained as an oil. Believing that it might be a labile form of phenyl isocrotonic acid, $C_6H_5CH=CHCH_2COOH$ (the normal reaction product if the $RMgX$ compound was truly the cinnamylmagnesium chloride postulated by Rupe and Bürgin), part of it was boiled gently in a test-tube to get α -naphthol. On cooling, a solid acid was obtained identical (by mixed melting point) with that described above; m. p., 135–136°. This acid was identified as methyl atropic acid by a mixed-melting-point determination with an authentic specimen prepared according to directions of Ogialoro¹² from sodium phenylacetate, paraldehyde and acetic anhydride. Its neutralization equivalent was 161 (calcd., 162). The oil may be a stereoisomer of the 135–136° solid.

In another run, the Grignard reagent was started with iodine and

⁹ Baeyer, *Ber.*, **38**, 2759 (1905).

¹⁰ A preliminary account of this and other means of activation was given in a paper presented at the Philadelphia meeting of the American Chemical Society, September 7, 1926. Mention of the alloy is contained in a recent paper by Hurd and Webb, *This Journal*, **49**, 546 (1927).

Bars or ingots of the 12.75% copper-magnesium alloy may be purchased from the American Magnesium Corporation at Niagara Falls, New York. The powdered alloy of 200 mesh is sold by the Eastman Kodak Co., Rochester, New York.

¹¹ Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

¹² Ogialoro, *Gazz. chim. ital.*, **15**, 514 (1885). Rupe, *Ann.*, **369**, 322 (1909).

moderate warming in the presence of a carbon dioxide atmosphere. The reaction was allowed to proceed at the boiling point of ether (due to the heat of reaction) and from a 0.2-mole run there was obtained 6.5 g., or a 20% yield of methyl atropic acid. There is then a restricted optimal temperature range, below which the reaction is virtually stopped, and above which the yield of acid drops.

Summary

Methyl atropic acid is obtained when cinnamyl chloride and carbon dioxide are added to magnesium in ether. The formation of this acid probably is due to the rearrangement of cinnamylmagnesium chloride.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SOME BROMINE DERIVATIVES OF PENTANOIC AND HEXANOIC ACIDS

BY R. MERCHANT, J. N. WICKERT AND C. S. MARVEL

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The ω -halogen derivatives of pentanoic and hexanoic acids are of some interest in connection with the preparation of compounds related to ornithine and lysine. Several methods of synthesis are already available but they are not entirely satisfactory in all details.

5-Bromopentanoic acid has been prepared by Cloves¹ by heating 5-phenoxy-pentanoic acid with concd. hydrobromic acid in a sealed tube at 145°. The 5-phenoxy-pentanoic acid is best prepared by Gabriel's method² from diethyl phenoxypropylmalonate. This ester has been described in several papers^{2,3} and the yields are said to be about 55% when γ -chloropropylphenyl ether is condensed with the sodium derivative of malonic ester.

All of these reactions have been reinvestigated and the methods and yields have been improved. Thus, in the preparation of diethyl phenoxypropylmalonate, the use of γ -bromopropylphenyl ether in place of the chloro compound has increased the yield of the ester to about 70–80%. The 5-phenoxy-pentanoic acid has been reacted with 48% hydrobromic acid without the use of sealed tubes to give better than 60% of the calculated amount of 5-bromopentanoic acid. A more direct preparation of this bromo acid was developed, in which the diethyl phenoxypropylmalonate was treated directly with 48% hydrobromic acid. The yield based on the ester is 65–69%.

¹ Cloves, *Ann.*, **319**, 367 (1901).

² Gabriel, *Ber.*, **25**, 418 (1892).

³ (a) Funk, *Ber.*, **26**, 2569 (1893). (b) Granger, *Ber.*, **28**, 1199 (1895). (c) Günther, *Ber.*, **31**, 2136 (1898).

2,5-Dibromopentanoic acid has been prepared previously from diethyl α,δ -dibromopropylmalonate by hydrolysis with concd. hydrobromic acid.⁴ It has been found that the bromination of 5-bromopentanoic acid in the presence of a small amount of phosphorus tribromide⁵ proceeds smoothly to give the 2,5-dibromo acid. An attempt was made to obtain this acid by first brominating phenoxypropylmalonic acid and then removing carbon dioxide and splitting the ether acid with hydrobromic acid. This method was not at all satisfactory. Apparently, bromine enters the benzene ring and the resulting mixture of products is very hard to purify. Practically no pure 2,5-dibromopentanoic acid could be isolated from this reaction.

In a previous paper⁶ from this Laboratory a solid compound thought to be 2,6-dibromohexanoic acid was described. It was prepared by the bromination of phenoxybutylmalonic acid, followed by the elimination of carbon dioxide and the splitting of the ether with hydrobromic acid. The compound was so different in its physical properties from those of the 2,5-dibromopentanoic acid prepared in this work that it was thought advisable to prepare a sample of 2,6-dibromohexanoic acid by the bromination of 6-bromohexanoic acid. This was done and the pure 2,6-dibromo acid was obtained as a heavy liquid. The compound previously described is undoubtedly not a simple hexanoic acid derivative.

The acid chlorides and ethyl esters of 5-bromopentanoic acid and of 2,5-dibromopentanoic acid have been prepared and are described in the Experimental Part.

Experimental Part

Diethyl Phenoxypropylmalonate.—The usual procedure for the alkylation of malonic ester was followed.⁷ The quantities used were 2.5 liters of absolute alcohol, 69 g. of sodium, 720 g. of diethyl malonate and 645 g. of γ -bromopropylphenyl ether. The product was collected at 185–189° (4 mm.). The yield varied from 615 to 710 g., or 70–80%. The product did not solidify at ordinary temperatures. Its purity was shown by the saponification number 148.6, whereas the calculated value is 147; d_{20}^{25} , 1.0858; n_D^{25} , 1.488; M_D calcd., 77.45; found, 78.00.

5-Phenoxypentanoic Acid.—This product was prepared by Gabriel's² method in yields of 87–93%, based on the ester. It boiled at 175° (4 mm.) and melted at 65–66°.

5-Bromopentanoic Acid from 5-Phenoxypentanoic Acid.—A 1-liter flask was fitted

⁴ (a) Willstätter and Ettlinger, *Ann.*, **326**, 101 (1903). (b) Fischer and Suzuki, *Ber.*, **37**, 2843 (1904).

⁵ Compare the method of Clarke and Taylor for α -bromocaproic acid, "Organic Syntheses," John Wiley and Sons, New York, 1925, vol. 4, p. 9.

⁶ Marvel, MacCorquodale, Kendall and Lazier, *This Journal*, **46**, 2842 (1924).

⁷ Ref. 5, p. 11.

by means of a ground-glass connection to a 1-meter fractionating tube leading to a condenser set for distillation. In this flask were placed 330 g. of 5-phenoxy-pentanoic acid and 500 cc. of 48% hydrobromic acid. The mixture was boiled over a flame at such a rate that the temperature at the head of the fractionating column was maintained at 115–120°, thus allowing water and phenol to distil out of the reaction mixture. The reaction was complete in five to eight hours, as no more phenol distilled. The reaction mixture was diluted with about 500 cc. of water and the 5-bromopentanoic acid was collected in ether. The ether extract was separated and evaporated and the residue was distilled under reduced pressure. The yield of acid boiling at 123–131°, at 6 mm., was 195–200 g., or 63–64%. On cooling, the product solidified; m. p., 38–39°.

5-Bromopentanoic Acid from Diethyl Phenoxypropylmalonate.—In the same way, 455 g. of diethyl phenoxypropylmalonate was treated with 300 cc. of 48% hydrobromic acid. The ester hydrolyzed and the ethyl alcohol was largely converted to ethyl bromide. Large quantities of carbon dioxide were evolved so that considerable foaming occurred in the early part of the reaction. When most of the ethyl bromide had distilled, another lot of 400 cc. of hydrobromic acid was added to the reaction mixture and the heating was then continued. When no more phenol distilled, the product was isolated as described before. The yield of pure acid, b. p. 142–145°, at 13 mm., was 182–193 g., or 65–69%; m. p., 38–39°.

Ethyl 5-Bromopentanoate.—Cloves¹ has esterified 5-bromopentanoic acid with ethyl alcohol, using dry hydrogen chloride as a catalyst. He collected and analyzed a fraction boiling at 120–176°, at 15 mm. No other physical properties were recorded.

A mixture of 50 g. of the bromo acid, 300 cc. of absolute alcohol and 5 g. of concd. sulfuric acid was refluxed for about two hours. The excess of alcohol was then distilled, the remaining crude ester dissolved in ether, washed with sodium carbonate solution and distilled. The yield of ester, b. p. 94–97°, at 7 mm., was 34–42 g., or 58–72%; d_4^{24} , 1.3191; n_D^{24} , 1.4580; M_D , calcd., 43.85; found, 43.23.

5-Bromopentanoyl Chloride.—A mixture of 50 g. of 5-bromopentanoic acid and 90 g. of thionyl chloride was refluxed for about two hours and then distilled. The yield of pure acid chloride, b. p. 102–104°, at 15 mm., was 45 g., or 80%; d_4^{27} , 1.5010; n_D^{26} , 1.4879; M_D , calcd., 37.93; found, 38.29.

Anal. Subs., 0.1192, 0.4283: 6.80, 24.65 cc. of 0.1737 *N* AgNO₃. Calcd. equivalents of halogen: 0.001196, 0.004284. Found. 0.001180, 0.004265.

When treated with 30 g. of absolute alcohol, the above acid chloride gave 42 g. of the ethyl ester; b. p., 106–110°, at 20 mm.; yield, 89%.

2,5-Dibromopentanoic Acid.—A mixture of 53 g. of 5-bromopentanoic acid and 0.5 cc. of phosphorus tribromide was placed in a flask fitted to a reflux condenser by means of a ground-glass joint. Through the condenser, 60 g. of dry bromine was added. Some hydrogen bromide was evolved at room temperature. The flask was placed in an oil-bath at 70–80° for about 15 hours and finally heated for a few minutes at 110° to drive out most of the dissolved hydrogen bromide. The material was then transferred to a Claisen flask and distilled under reduced pressure. The yield of dibromo acid, b. p. 150–152°, at 5 mm., was 69 g., or 91%. The boiling point given in the literature^{4b} is 171–174°, at 13–15 mm. The neutral equivalent for the acid prepared above was found to be 261; calcd., 260; d_4^{25} , 1.8629; n_D^{25} , 1.5347; M_D , calcd., 42.47; found, 43.42.

2,5-Dibromopentanoyl Chloride.—In a flask fitted to a reflux condenser by means of a ground-glass joint was placed 150 g. of 5-bromopentanoyl chloride. Through the condenser 160 g. of dry bromine was added, over a period of two hours. The mixture was heated overnight on a steam-bath and then distilled under reduced pressure. Some

unchanged 5-bromopentanoyl chloride distilled first and then the dibromo acid chloride was collected at 138–145°, at 15 mm.; yield, 162 g., or 77%. The boiling point reported here is somewhat higher than that given by Fischer and Suzuki.^{4b}

Ethyl 2,5-Dibromopentanoate.—A mixture of 430 g. of 5-bromopentanoic acid and 275 g. of thionyl chloride was allowed to react and the excess of thionyl chloride was then distilled. The residue was brominated with 420 g. of dry bromine. The crude 2,5-dibromopentanoyl chloride thus obtained was treated with 350 cc. of absolute ethyl alcohol. The ester was distilled under reduced pressure. The yield of ester, b. p. 128–135°, at 14 mm., was 400 g., or 58%. On redistillation most of the product boiled at 133–135°, at 14 mm.; d_4^{25} , 1.6289; n_D^{25} , 1.4947, M_D , calcd., 50.51. Found. 51.53.

Anal. Subs., 0.4516, 0.4182: 18.00, 16.77 cc. of 0.1737 *N* AgNO₃. Calcd. for C₇H₁₂Br₂O₂: Br, 55.6. Found: 55.4, 55.4.

6-Bromohexanoic Acid.—A mixture of 153 g. of diethyl phenoxybutylmalonate and 500 cc. of 48% hydrobromic acid was treated as described for the preparation of 5-bromopentanoic acid. The yield of product, b. p. 160–168°, at 18 mm., was 60 g., or 62%.

2,6-Dibromohexanoic Acid.—The general procedure used was that described for the bromination of 5-bromopentanoic acid. From 25 g. of 6-bromohexanoic acid, 24 g. of dry bromine and 3 cc. of phosphorus tribromide, there was obtained 28 g., or 80%, of 2,6-dibromohexanoic acid; b. p., 158–160°, at 4 mm.; n_D^{21} , 1.5245, d_4^{21} , 1.7897; M_D , calcd., 47.09; found, 46.88.

Anal. Subs., 0.1954, 0.2492: 8.23, 10.49 cc. of 0.1737 *N* AgNO₃. Calcd. for C₆H₁₀O₂Br₂: Br, 58.39. Found: 58.53, 58.50.

Summary

1. Improved methods for the preparation of 5-bromopentanoic acid and 2,5-dibromopentanoic acid and their esters and acid chlorides have been described.

2. It has been shown that the earlier description of 2,6-dibromohexanoic acid is in error and the correct description of this compound has been given.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]
THE ALKALINE OXIDATION OF ALPHA-NITRONAPHTHALENE

BY JOHN H. GARDNER¹

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Since it has been known for a long time that in the oxidation of α -nitronaphthalene in an acid medium, 3-nitrophthalic acid is the principal product,² it seemed logical to expect that the oxidation with alkaline permanganate should yield a nitrophthalonic acid, which could be converted into 3- or 6-nitrophthalaldehyde acid by procedure analogous to that used by Fuson³ for the preparation of phthalaldehyde acid from phthalonic acid. On carrying out the oxidation, however, it was found that the nitrated ring was attacked.

¹ National Research Fellow in Chemistry.

² Beilstein and Kurbatow, *Ann.*, **202**, 217 (1880).

³ Fuson, *THIS JOURNAL*, **48**, 1093 (1926).

α -Nitronaphthalene was oxidized by alkaline permanganate according to the same procedure that was used by Fuson for the oxidation of naphthalene. The product was condensed with aniline producing a derivative which, by melting point and analysis, was found to be identical with that obtained from phthalonic acid. This was further confirmed by its decomposition into the aniline derivative of phthalaldehyde acid and the preparation from that of phthalaldehyde acid itself.

This is not so surprising as it appears at first sight, since a similar result has been obtained in the case of other positively substituted naphthalene derivatives. For example, Graebe has shown that in the oxidation of α -naphthoylbenzoic acid and 1,2-benzanthraquinone, the ring of the naphthalene residue attached to the carbonyl groups is oxidized.⁴ This reaction has been confirmed in the second case by Scholl and Schwinger, who also pointed out that in an acid medium 1,2-benzanthraquinone is oxidized to anthraquinone-1,2-dicarboxylic acid, thus showing a complete parallel with the oxidation of α -nitronaphthalene.⁵

The production of a pronounced yellow color on boiling a suspension of α -nitronaphthalene in a solution of sodium hydroxide indicates the possibility of a reaction between the two. At present, however, there is no information available to justify any conclusion as to the nature of the reaction.

Experimental Part

Oxidation of α -Nitronaphthalene.—To a boiling mixture of 43 g. of α -nitronaphthalene and 500 cc. of 0.5 *N* sodium hydroxide solution in a flask provided with a reflux condenser and an efficient mechanical stirrer, there was added in small portions a boiling solution of 212 g. of potassium permanganate in 1500 cc. of water, during a period of one and one-half hours. The mixture was maintained at the boiling temperature until half an hour after the last addition of permanganate. A little alcohol was then added to destroy any remaining permanganate, and the mixture cooled and filtered. The filtrate was acidified with 140 cc. of concd. hydrochloric acid and evaporated to 500 cc. One hundred g. of aniline was then added and the resulting solution heated on the water-bath for two hours. After cooling, the crystalline precipitate was filtered out and dried at room temperature. Drying at an elevated temperature was found to cause considerable decomposition. The yield was 67 g., or 74%.

After several recrystallizations from alcohol, using Norite the first time, the product melted at 162–164°, with decomposition.

All melting points recorded in this paper are corrected.

Fuson reports³ for the aniline derivative of phthalonic acid, 165°. A mixed melting point of the product from α -nitronaphthalene with the aniline derivative of phthalonic acid showed no depression.

Anal. Subs., 0.3397, 0.3549: 40.60, 40.00 cc. of 0.1016 *N* HCl; 16.55, 16.10 cc. of 0.1328 *N* NaOH. Calcd. for $C_{21}H_{19}O_4N_2$: N, 7.73. Found: 7.94, 7.60.

Decomposition of the Aniline Derivative Obtained from the Oxidation Product of α -Nitronaphthalene.—Twenty-two g. of the aniline derivative was suspended in

⁴ Graebe, *Ann.*, **340**, 249 (1905).

⁵ Scholl and Schwinger, *Ber.*, **44**, 2992 (1911).

150 cc. of sodium-dried xylene and boiled under reflux for one and one-half hours. On cooling, there was deposited 13.2 g. of a gray powder.

On boiling the decomposition product with alcohol, 4 g. of a gray powder, softening at about 259°, remained undissolved. A similar by-product was noted in the preparation of the aniline derivative of phthalaldehyde acid by Fuson's procedure.

The alcoholic solution, after treatment with Norite, on cooling, deposited almost microscopic, colorless needles; m. p., 178°. The aniline derivative of phthalaldehyde acid melted at 176–177°. A mixed melting point showed no depression.

Anal. Subs., 0.3770, 0.3320: 30.35, 30.20 cc. of 0.1016 *N* HCl; 11.10, 12.00 cc of 0.1328 *N* NaOH. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: 5.98, 5.94.

Preparation of Phthalaldehyde Acid.—For the preparation of phthalaldehyde acid, 44 g. of the aniline derivative of phthalonic acid, obtained from α -nitronaphthalene, was decomposed as described above. The xylene was decanted as completely as possible, and the residue boiled under reflux with 350 cc. of 10% hydrochloric acid for one and one-half hours. After cooling, the solution was filtered from a small amount of insoluble material and extracted with ether. The ether was evaporated and the residue dissolved in water. After treatment with Norite, the solution was evaporated to dryness, as the attempt to induce crystallization failed. The residue melted at 96° and showed no depression in melting point when mixed with phthalaldehyde acid. The product was free from nitrogen.

Neutral equivalent. Subs., 0.4277, 0.4177: 20.95, 20.59 cc. of 0.1328 *N* NaOH. Calcd. for $C_8H_6O_3$: neut. equiv., 150. Found: 153.7, 152.8.

Summary

It has been shown that in the oxidation of α -nitronaphthalene by potassium permanganate in an alkaline medium, the nitrated ring is attacked.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A SYNTHESIS OF TAURINE

BY C. S. MARVEL, C. F. BAILEY AND M. S. SPARBERG

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Taurine, 2-amino-ethylsulfonic acid, is of considerable interest to the physiological chemist since it occurs in the tissues of various lower animals and in secretions of the higher animals. In the bile it is found combined with cholic acid as taurocholic acid. The probable source of natural taurine is the amino acid, cystine. This conversion of cystine to taurine has been carried out in the laboratory by Friedmann¹ but it does not furnish a practical method of preparation.

At present the common sources for taurine are ox bile² and the large muscle of the abalone.³ The first source gives a very low yield of the

¹ Friedmann, *Beitr. Phys. Path.*, **3**, 38 (1903).

² (a) Hammersten, *Z. physiol. Chem.*, **32**, 456 (1901); (b) Tauber, *Beitr. Phys. Path.*, **4**, 324 (1904).

³ Schmidt and Watson, *J. Biol. Chem.*, **33**, 499 (1918).

product, and large amounts of the starting material must be available if any considerable amount of taurine is needed. The second source is said to be very satisfactory and 74 kg. of the muscles will yield 362 g. of taurine.

Taurine has been synthesized by several methods. Kolbe⁴ converted isethionic acid, $\text{HOCH}_2\text{CH}_2\text{SO}_3\text{H}$, to 2-chloro-ethylsulfonyl chloride, hydrolyzed this product to 2-chloro-ethylsulfonic acid and obtained taurine from this by the action of aqueous ammonia. However, he was troubled with the separation of the taurine from the ammonium chloride. Anschütz⁵ has also used this general method.

Gabriel⁶ prepared taurine from ethylene imine and sulfur dioxide and from 2-mercaptothiazoline⁷ by oxidation with bromine water. More recently Reychler⁸ obtained taurine from bromo-ethylamine and ammonium sulfite. All of these methods require 2-bromo-ethylamine as a starting material and are not really useful for the preparation of any large amount of product.

Auzies⁹ reports the preparation of taurine by sulfonation of acetaldehyde with chlorosulfonic acid, followed by the formation first of the aldehyde ammonia, then of the imido compound and finally by reduction to the amino compound. The reactions are quite complex.

Some time ago Kohler¹⁰ mentioned that the sodium salt of 2-bromo-ethylsulfonic acid was easily obtained from ethylene bromide and sodium sulfite. No details of the reaction were given but a statement was made that the compound would be described later. However, a search of the literature has not revealed any further information concerning this compound. This seemed to be a suitable starting point for the synthesis of taurine, so the preparation was studied and found to run very smoothly and in yields of about 80%.

In the first attempts to convert sodium 2-bromo-ethylsulfonate into taurine a method very much like that described by Kolbe⁴ was used. 2-Bromo-ethylsulfonyl chloride was prepared and then hydrolyzed to the acid. The sulfonic acid was then treated with aqueous ammonia and after the reaction was complete the taurine separated by crystallization from dilute alcohol which readily held in solution the ammonium bromide produced in the reaction. The yields by this procedure were very low.

It was then found that the sodium salt or the 2-bromo-ethylsulfonic acid could be treated directly with aqueous ammonia to give a mixture

⁴ Kolbe, *Ann.*, **122**, 42 (1862).

⁵ Anschütz, *Ann.*, **415**, 97 (1918).

⁶ Gabriel, *Ber.*, **21**, 2667 (1888).

⁷ Gabriel, *Ber.*, **22**, 1153 (1889).

⁸ Reychler, *Bull. soc. chim. Belg.*, **32**, 247 (1923).

⁹ Auzies, *Chem. Zentr.*, **82** [II], 1433 (1911).

¹⁰ Kohler, *Am. Chem. J.*, **20**, 692 (1898).

of taurine and sodium bromide from which pure taurine could be easily obtained by crystallization from about 80% alcohol. The yield of product is about 40–50%. Undoubtedly, a considerable loss occurs in the separation from the sodium bromide.

The reaction between aqueous ammonia and sodium 2-bromo-ethyl-sulfonate is much slower than might be predicted from the relative positions of the bromine and the sulfur atoms. Several days are required for the complete conversion of the bromo to the amino compound. This is in accord with the results of Helfrich and Reid,¹¹ who have shown that oxidation of dichloro-ethyl sulfide to the sulfoxide and sulfone produces compounds with less active chlorine.

Experimental Part

Sodium 2-Bromo-ethylsulfonate.—In a 5-liter flask fitted with a reflux condenser, mechanical stirrer and separatory funnel were placed 615 g. of ethylene dibromide, 1250 cc. of 95% alcohol and 450 cc. of water. The stirrer was started and the mixture was heated to boiling. To the well-stirred, boiling mixture a solution of 125 g. of sodium sulfite (anhydrous salt) in about 450 cc. of water was added through the separatory funnel over a period of about two hours. The solution was boiled under a reflux condenser for two hours after all of the sulfite solution had been added and then the condenser was set for distillation and the alcohol and ethylene bromide were distilled. The remaining water solution was poured into a large evaporating dish and evaporated to dryness on the water-bath. The sodium 2-bromo-ethylsulfonate was extracted from the sodium bromide and unchanged sodium sulfite with 2 liters of boiling 95% alcohol. On cooling the solution, most of the salt crystallized and the mother liquor was used for a second extraction of the residue. The product after one crystallization from alcohol was dried in an oven at 110°; yield, 165–190 g., or 78–90%.

This product may contain as much as 5–8% of sodium bromide, but this does no harm in the subsequent reactions. The amount of sodium bromide can be estimated by titrating a sample of the salt with standard silver nitrate solution.

The concentration of alcohol seems to be fairly important and poorer yields were obtained when it was changed in either direction. The large excess of ethylene bromide is necessary to avoid the formation of the disulfonic acid. By diluting the alcoholic solution distilled after the reaction is finished, it is possible to recover nearly 400 g. of ethylene bromide. The salt is slightly hygroscopic and should be dried in an oven in order to remove the last of the water.

2-Bromo-ethylsulfonyl Chloride.—In a 1-liter round-bottomed flask fitted with a stopper carrying a calcium chloride tube were placed 100 g. of sodium 2-bromo-ethyl-sulfonate and 100 g. of phosphorus pentachloride. The reaction proceeded quietly and the contents of the flask became semi-fluid. After the reaction seemed to have stopped, the mixture was heated on a steam-bath for about two or three hours to insure complete reaction. It was then cooled thoroughly in an ice-salt mixture and treated with about 500 cc. of ice water to dissolve the salts and decompose any excess of phosphorus pentachloride. The oily layer, consisting of the sulfonyl chloride and considerable phosphorus oxychloride, was separated and distilled under reduced pressure. The yield of light straw-colored product, b. p. 119–121° at 25 mm., was 62–70 g., or 64–71%.

Anal. (Stepanow). Subs., 0.4157: 39.59 cc. of 0.1 *N* AgNO₃. Calcd. for C₂H₄O₂ClBrS: 40.06 cc. D₂₀²⁰, 1.921; *n*_D²⁰, 1.5242.

¹¹ Helfrich and Reid, *THIS JOURNAL*, **42**, 1208 (1920).

The product has a disagreeable odor and is a lachrymator. It hydrolyzes rather easily in the presence of water.

Taurine from 2-Bromo-ethylsulfonyl Chloride.—Thirty-seven g. of the sulfonyl chloride was added to 600 cc. of cold water and allowed to stand until the oily layer disappeared. It was then evaporated under reduced pressure to remove the water and hydrogen chloride. The residue (usually about 25 cc.) was treated with 150 cc. of aqueous ammonia (d., 0.9) and allowed to stand for several days. Then the dark colored solution was boiled with decolorizing carbon (Norite), filtered and evaporated to 10–15 cc., until no odor of ammonia was perceptible. On the addition of 95% alcohol, taurine crystallized; yield, about 3.5 g., or 16%.

Anal. (Kjeldahl). Subs., 1.3706: 10.77 cc. of 1 *N* acid. Calcd. for $C_2H_7O_2NS$: N, 11.2. Found: 11.0.

The Reaction between Sodium 2-Bromo-ethylsulfonate and Aqueous Ammonia.—In order to find out the approximate rate of reaction between sodium 2-bromo-ethylsulfonate and aqueous ammonia, a weighed sample of the dry salt was dissolved in a large excess of aqueous ammonia and from time to time aliquot portions were titrated with standard silver nitrate solution to determine the amount of bromide ion. These experiments indicated that the reaction was about 25% complete in five hours, 60% complete in thirty hours and 90% complete in five days. The reaction did not seem to have proceeded further at nine days, so in subsequent experiments five days were allowed for this reaction.

The reaction between sodium 2-bromo-ethylsulfonate and ammonia might produce taurine and sodium bromide, or the sodium salt of taurine and ammonium bromide. In order to determine which products were produced, some samples of the sulfonic acid salt and ammonia were allowed to stand for five days and then evaporated to dryness. When all of the excess of ammonia had been driven off, the residue was analyzed by the Kjeldahl method. This residue would contain twice as much nitrogen if the sodium salt of taurine and ammonium bromide were formed as it would if taurine and sodium bromide were formed. The actual amount of nitrogen was always somewhat less than that required for the second reaction.

Taurine from Sodium 2-Bromo-ethylsulfonate.—A solution of 110 g. of sodium 2-bromo-ethylsulfonate (containing 5–6% of sodium bromide) in about 2 liters of concd. aqueous ammonia (d., 0.9) was allowed to stand for five to seven days and then evaporated to dryness. The last of the water was removed by heating on a steam-bath. The residue was dissolved in the minimum amount of hot water and, if necessary, treated with decolorizing carbon (Norite). The colorless solution was concentrated to 65–70 cc. and about four volumes of 95% alcohol were added. In a short time taurine mixed with some sodium bromide separated. When crystallization was complete, the crude taurine was collected on a filter and recrystallized by dissolving in hot water and then adding to the solution enough 95% alcohol to give a final concentration of 80% of alcohol. The taurine which then separated was usually free from bromides. However, occasional runs had to be recrystallized four or five times to remove all of the sodium bromide. The yield of pure taurine was 31 to 36 g., or 44–51%.

Summary

Taurine, 2-amino-ethylsulfonic acid, has been prepared in fair yields by converting ethylene bromide to sodium 2-bromo-ethylsulfonate and treating this product with aqueous ammonia.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA. V. PRIMARY, SECONDARY AND TERTIARY ALKYL AMINES

BY FREDERICK K. BELL¹

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Introduction

All of the ammonia derivatives thus far examined in this series of studies² contained the aryl group and, with the exception of the phenyl amines and naphthylamine, were of the mixed aryl-alkyl type.

The present communication is concerned with the examination of the purely aliphatic amines. It was hoped that the results of this investigation, in conjunction with those already obtained in the case of the pure aryl amines, would be of assistance in the interpretation of the absorption spectra of the mixed amines previously examined. This expectation has been at least partially fulfilled.

The absorption spectra, between 1.0 and 12.0 μ , of three series (*n*-propyl, *n*-butyl and *iso*-amyl) of primary, secondary and tertiary amines are presented and discussed in this communication.

Experimental Part

The same experimental procedure as previously described has been followed in the present work. Since all of the substances examined are liquids, the measurements were made at room temperature. In this connection it appears desirable to mention a precaution which should be taken in the examination of liquids in the open type of absorption cell as employed in this work. Considerable evaporation of the liquid may take place depending, of course, on the boiling point of the liquid in question, and liquid must be added from time to time in the course of the examination. This procedure was found to be necessary in the case of several compounds in the present study.

The specimens of mono-, di- and tri-*n*-propylamine, mono-, di- and tri-*n*-butylamine and mono-, di- and tri-*iso*-amylamine were obtained from

¹ E. R. Squibb and Sons Fellow.

² Bell, *THIS JOURNAL*, (a) **47**, 2192, 3039 (1925); (b) **48**, 813, 818 (1926).

the Eastman Kodak Company. They were labeled "highest purity" and were used as obtained in original glass-sealed containers.

The absorption spectra of these compounds are shown graphically in Figs. 1 to 9, in which the percentage transmission has been plotted against the wave length in microns. In every case the thickness of the absorbing layer was 0.025 mm., as indicated on each curve by the value of T .

Discussion

The infra-red absorption spectrum of only one of the simple alkyl amines has been recorded in the literature, namely, triethylamine, in Coblenz' monograph.³

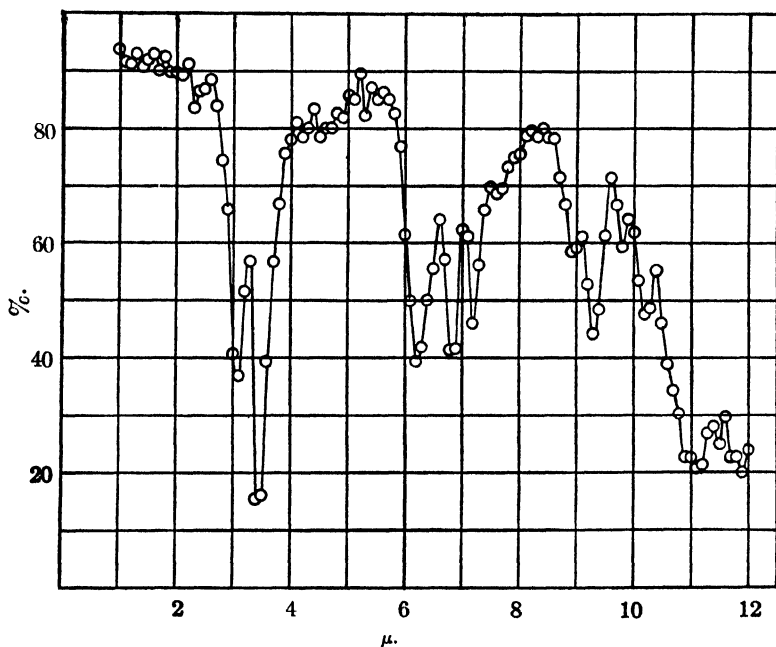


Fig. 1.—*n*-Propylamine; $T = 0.025$ mm.

The curves in Figs. 1 to 9 show certain general similarities. The general transparency of the nine substances is of the same order of magnitude, with the possible exception of di-*n*-butylamine. However, between 10.0 and 12.0 μ the three mono derivatives (Figs. 1, 4 and 7) show a marked similarity in opacity, as contrasted with the relatively high degree of transparency of the other derivatives in the same region. No definite influence which can be attributed to increase in molecular weight is to be noticed.

³ Coblenz, *Carnegie Inst. Pub.*, 35, 63 (1905).

In the region of 3.45μ , the characteristic band of the methyl group is sharply defined in each case with marked regularity in intensity. Similarly, in each curve there appears a band of diminished intensity at 6.85μ . Coblentz found this band in numerous compounds of different chemical structure. If we assume an harmonic relation between this band and the 3.45μ band, its presence is to be attributed to the same origin, that is, the methyl group.

It will be noticed also that a sharply defined band appears in each curve in the region of 7.25μ , its position varying from 7.2 to 7.3μ . With the possible exception of a band appearing with a fair degree of constancy

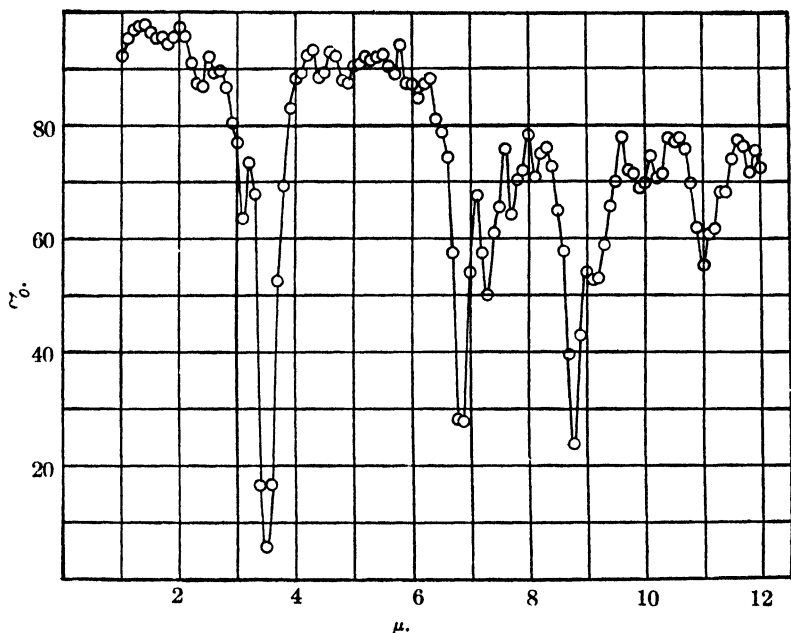


Fig. 2.—Di *n*-propylamine, $T = 0.025$ mm.

in the region of 9.3μ , no consistent similarity of the absorption curves is apparent in the longer wave lengths. This 9.3μ band was found consistently by Coblentz in his examination of petroleum distillates.³

As in the case of all of the ammonia derivatives which have been previously examined, the region between 3.0 and 4μ is of particular interest in the present study also. As has been noted above, the 3.45μ band remains strikingly constant in intensity, which appears to be independent of the molecular weight of the substituent alkyl group and also the number of hydrogen atoms of the ammonia molecule which have been substituted.

In the three primary amines (*n*-propyl, *n*-butyl and *iso*-amyl), the ammonia band is sharply resolved at 3.05μ , its intensity being less than

that of the 3.45μ band in each case. In the secondary amines (Figs. 2, 5 and 8), its location remains unchanged but its intensity is markedly decreased. This band has practically disappeared in the curves for the three tertiary amines (Figs. 3, 6 and 9) and is also absent in Coblenz' curve for triethylamine.

It is thus seen that the qualitative differentiation between primary and secondary and tertiary amines, as previously found, is valid in the case of the alkyl amines.

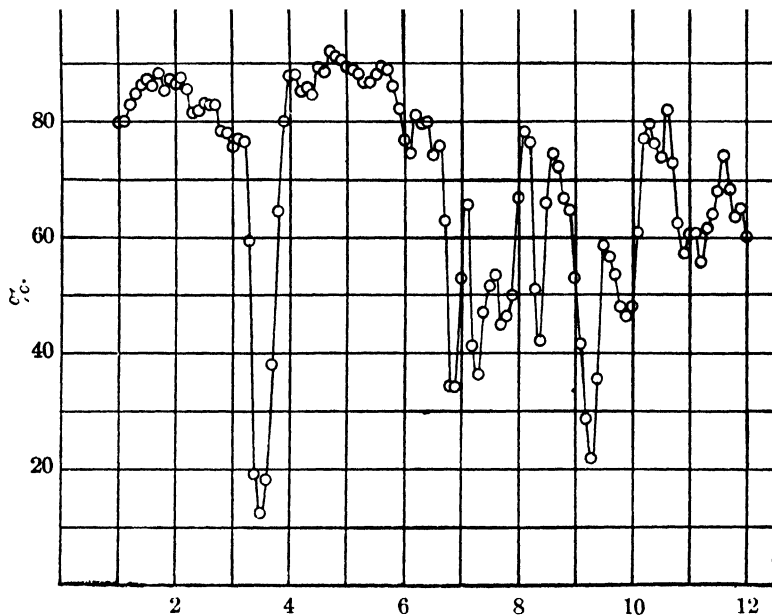


Fig. 3—Tri-*n*-propylamine; $T = 0.025$ mm.

Salant⁴ has examined the absorption spectra of di- and tri-*n*-propylamine, di- and tri-*n*-butylamine and di- and tri-*iso*-amylamine in the restricted region of 2.5 to 4.0μ . In that region of the present curves, there is good agreement with his measurements. It is apparent, however, that Salant used considerably thicker layers of the absorbing materials than those employed in the present study.

Another region of interest in the absorption spectra of the alkyl amines is at 6.25μ . In an earlier communication it was suggested that the^{2a} deep ammonia band, which Coblenz locates at 6.1μ , was also present in the spectra of organic derivatives of ammonia. It was pointed out that the absorption in that region cannot be readily interpreted when the benzene nucleus is present, since that nucleus has a characteristic ab-

⁴ Salant, *Proc. Nat. Acad. Sci.*, **12**, 74 (1926).

sorption at 6.25μ . In the present curves it is to be expected that the conditions in that region are greatly simplified.

In the case of the three primary amines (Figs. 1, 4 and 7) a well-defined band appears at 6.25μ , while the secondary and tertiary amines in Figs. 2, 3, 5, 6, 8 and 9 (and also in Coblenz' curve for triethylamine) show very little or no characteristic absorption at that point. There is, therefore, a marked diminution in the intensity of this band in passing from the primary to the secondary alkyl amine, but a slight change or none is to be noticed in the transition from the secondary to the tertiary amine; the examination of thicker layers of these substances might reveal a more pronounced difference.

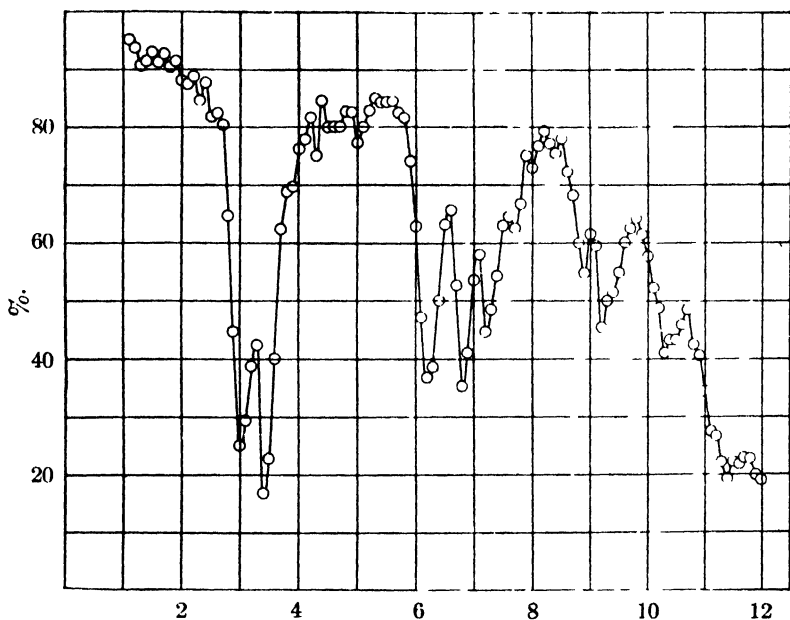


Fig. 4—*n*-Butylamine; $T = 0.025$ mm.

Salant, assuming the presence of the 6.1μ ammonia in amines,⁴ suggests that the 3.0μ ammonia band is the first harmonic of the 6.1μ band. Ellis,⁵ on the other hand, has shown, from his examination of aniline and ten mono- and dialkyl anilines as far as 2.8μ , that absorption bands occurring at 1.47μ and 1.04μ are characteristic of the nitrogen to hydrogen bond and that the vibrations corresponding to these two bands and that at 2.8μ , as found by the present author in an examination of the same compounds, form a three-membered parabolic series.

If we assume a shifting of the 6.1μ ammonia band to 6.25μ , the absorp-

⁵ Ellis, *THIS JOURNAL*, 49, 347 (1927).

tion curves of *n*-propyl, *n*-butyl and *iso*-amylamine confirm Salant's hypothesis. However, a more thorough examination of the secondary and tertiary alkyl amines in this region will be necessary in order to demonstrate definitely the presence or absence of characteristic absorption.

For present purposes, the significance of the 6.25μ band is quite definite. The absorption in this region permits a ready differentiation between mono-alkyl amines and di- or tri-alkyl amines. This differentiation should be especially useful in the examination of those compounds which contain the hydroxyl group, which has a pronounced characteristic absorption at 3.0μ . An instance of the complications that may exist in this region (3.0μ) is shown by the author's absorption curves of the alkaloids containing the tropan nucleus.⁶

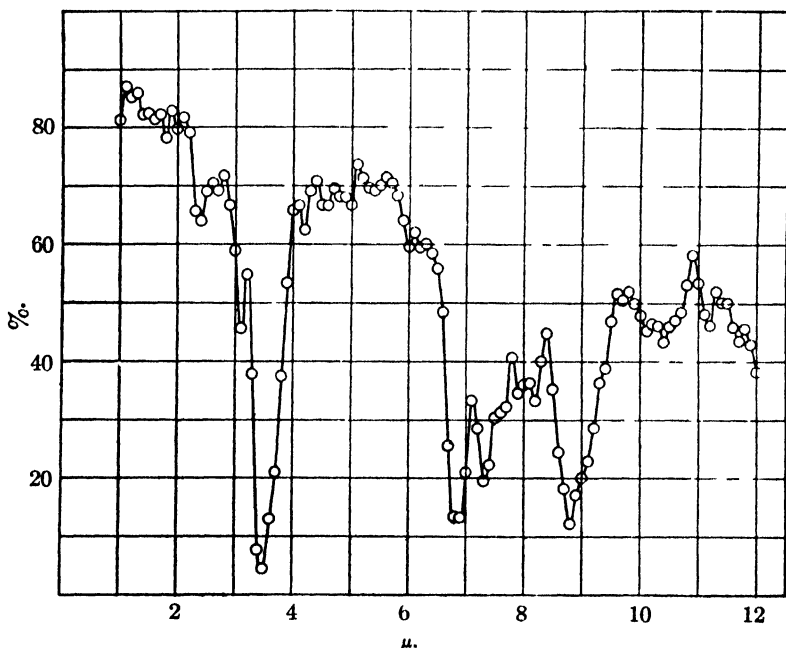
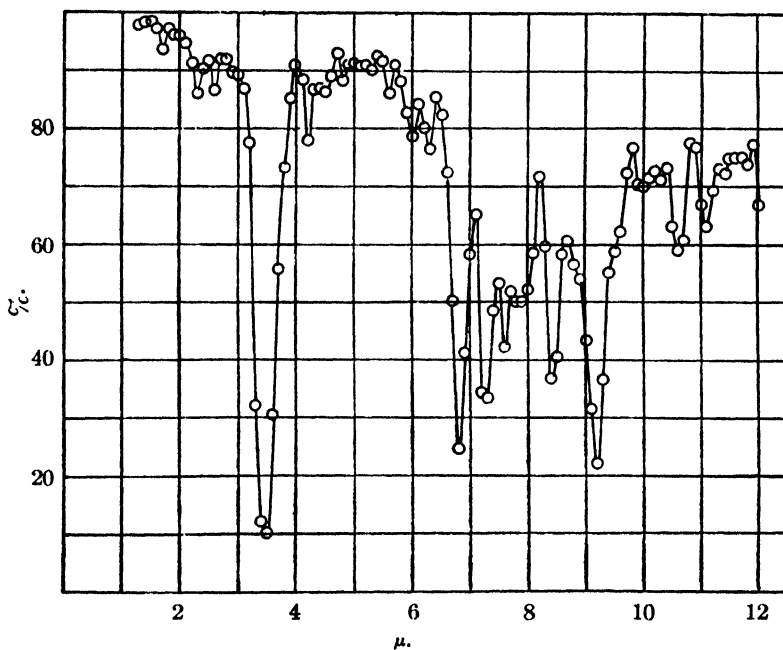
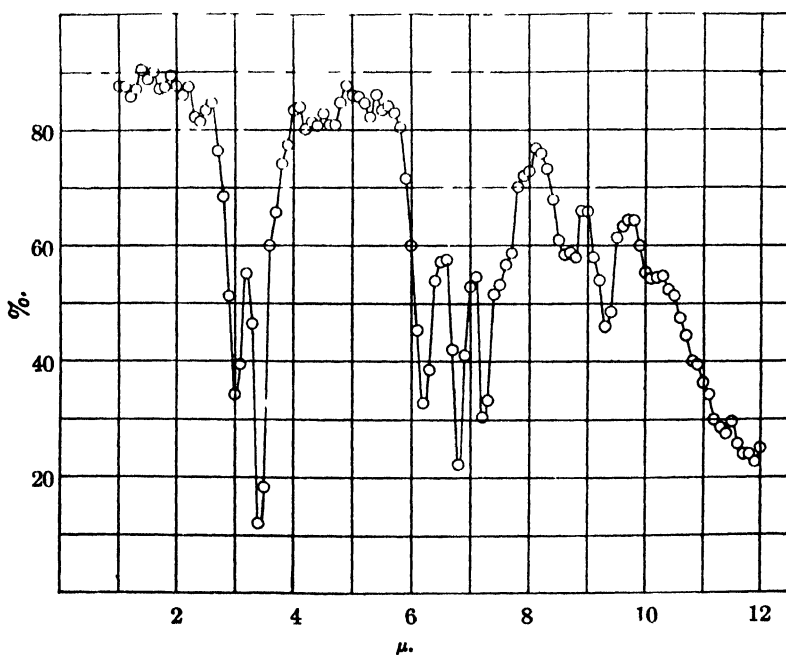


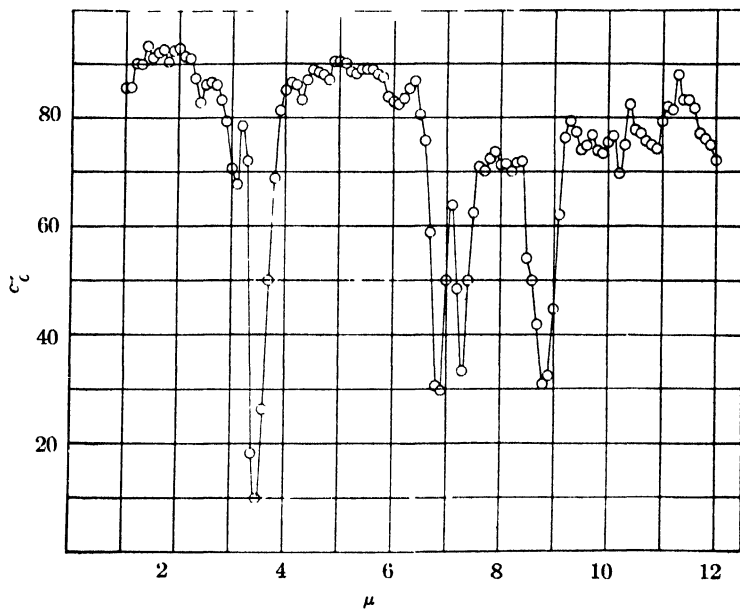
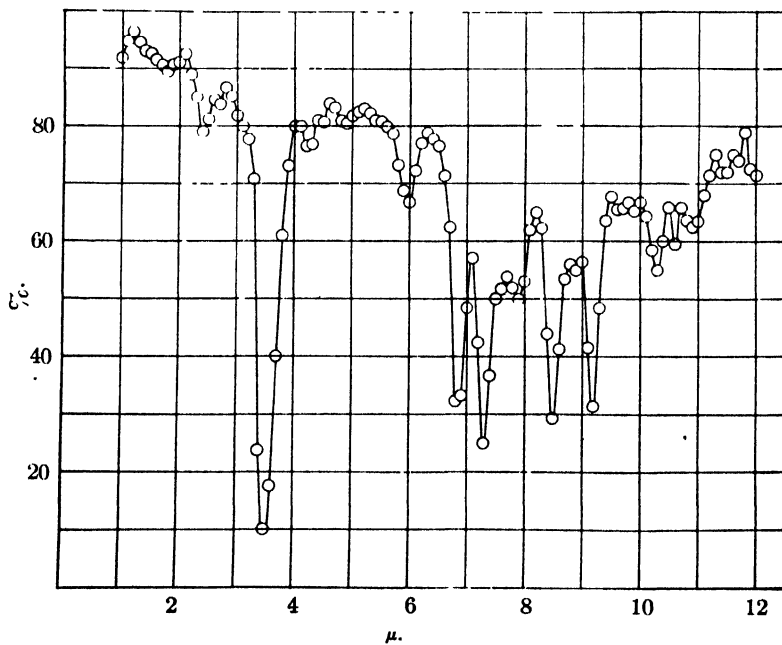
Fig. 5.—Di-*n*-butylamine, $T = 0.025$ mm.

Since the publication of the preceding paper of this series, it has come to the author's attention that a number of pertinent communications by Bonino had been inadvertently overlooked. Bonino⁷ suggests that the absorption occurring between 2.5 and 3.9μ is caused by linear oscillators formed of hydrogen atoms which oscillate around their position of equilibrium. If the hydrogen is united to one atomic species, for

⁶ Bell, *J. Pharmacol.*, 29, 533 (1926).

⁷ Bonino, *Gazz. chim. ital.*, 53, 555, 575, 583, 591 (1923); 54, 357, 465 (1924); 55, 335, 341, 576 (1925); 56, 278, 286, 292, 296 (1926).

Fig. 6.—Tri-*n*-butylamine; $T = 0.025$ mm.Fig. 7.—Iso-amylamine; $T = 0.025$ mm.

Fig. 8 —Di-iso amylamine, $T = 0.025$ mm.Fig. 9.—Tri-iso-amylamine; $T = 0.025$ mm.

example, carbon, oxygen or nitrogen, a simple band of constant location results, as in methane, water or ammonia. On the same basis, we should expect the presence of two bands in this region for such compounds as methyl alcohol or methylamine.

In his examination of the infra-red absorption spectra of halogen derivatives of ethylene and ethane (in which the number of carbon atoms is constant), Bonino found that the absorption band was always at 3.51μ . Its intensity varied, however, and it was entirely absent in tetrachloroethylene and hexachloro-ethane; furthermore, he observed that the coefficient of maximum absorption of this band follows quantitatively the variation in the number of hydrogen atoms, independently of the number of carbon atoms present. The exact location of this band in compounds of different chemical composition is determined, according to Bonino, by intermolecular action.

That these conclusions, developed by Bonino specifically for the case of the carbon to hydrogen bond, are likewise applicable to the nitrogen to hydrogen bond, as suggested by him, appears to be substantiated, at least qualitatively, by the experimental data of this series of studies. Preliminary work by the present author on the examination of some alkyl and aryl mercaptans, sulfides and disulfides points to a similar behavior for the hydrogen to sulfur bond.

Summary

1. The infra-red absorption spectra of mono-, di- and tri-*n*-propylamine, mono-, di- and tri-*n*-butylamine and mono-, di- and tri-*iso*-amylamine have been examined between 1.0 and 12.0μ .
2. The qualitative differentiation between primary and secondary and tertiary amines, by means of the intensity of the characteristic absorption band in the region of 3.0μ , has been found to be valid in the case of the alkyl amines.
3. Primary alkyl amines may be qualitatively differentiated from secondary or tertiary alkyl amines by the absorption in the region of 6.2μ . The significance of this differentiation, which fails in the presence of the aryl group, has been indicated.

BALTIMORE, MARYLAND

NOTES

A Grignard Starter.—Very often when preparing a Grignard reagent, addition of the halide fails to start the reaction. This is true of readily prepared reagents.

The writer has been quite successful in touching off such reaction mixtures by adding a small grain of anhydrous aluminum bromide. The bromide is quickly prepared by warming a few grains of aluminum in a

dish and pouring in some bromine, again warming to volatilize the excess. The mixture glows and fumes and the product must be used immediately. Anhydrous aluminum chloride¹ has also been successfully employed a few times.

The method has not been applied to any of the very difficult preparations.

CONTRIBUTION FROM THE
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RECEIVED APRIL 28, 1927
PUBLISHED JULY 5, 1927

The Chloromethylacetophenones.—In connection with some work on the condensation of benzil and substituted acetophenones, we have had occasion to prepare the 2-chloro-5-methyl and 4-chloro-3-methyl derivatives from *p*-chlorotoluene and *o*-chlorotoluene, respectively. These ketones have been reported once previously by Claus.¹ He made them by the action of acetyl chloride on the chlorotoluene in the presence of anhydrous aluminum chloride; his yields were very poor and the ketones boiled over a considerable range; furthermore, he did not analyze them because he realized they were impure. He made the oximes, however, and proved the structure of the ketones by oxidation to the corresponding chlorotoluic and chlorophthalic acids.

By the use of acetic anhydride instead of acetyl chloride² we have obtained the ketones nearly constant boiling after one distillation, the 3-chloro-4-methyl derivative in a yield of 70% and the 2-chloro-5-methyl derivative in a yield of 34%. Claus had great difficulty in preparing even small amounts of the latter. We have determined the boiling points and refractive indices of both the ketones; they distil without decomposition at atmospheric pressure, forming colorless oils that very slowly take on a yellow tinge in the light. They have a very faint odor suggestive of acetophenone.³

Ketones	B. p., °C.	Press., mm.	n_D^{25}	Anal.			
				Calcd. C, %	Calcd. H, %	Found C, %	Found H, %
2-Chloro-5-methylacetophenone	245.8–246.0	760.1	1.5419	64.1	5.3	63.9	5.4
4-Chloro-3-methylacetophenone	254.2–254.4	753.4	1.5521	64.1	5.3	64.0	5.3

CONTRIBUTION FROM THE
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RECEIVED MAY 10, 1927
PUBLISHED JULY 5, 1927

¹ Hesse, *Ber.*, **39**, 1127 (1906).

² Claus, *J. prakt. Chem.*, [2] **43**, 356 (1890); **46**, 26 (1892).

³ Noller with Adams, *THIS JOURNAL*, **46**, 1889 (1924).

⁴ The boiling points were determined with the mercury column of the thermometer wholly immersed in the vapor.

NEW BOOKS

Old Chemistries. By EDGAR F. SMITH, University of Pennsylvania. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City, 1927. xi + 89 pages, 32 illustrations. 26 × 18.5 cm. Price \$2.50.

The chemists who have had the good fortune to read this latest volume by Professor Smith have no doubt been tempted, as was the reviewer, to alter the old familiar motto of Alonzo of Aragon into "Old wood to burn, old wine to drink, old friends to trust and old chemistries to read." It is indeed just such a book as one would delight to discuss with a well-trying friend on a wintry evening when the wood fire is blazing merrily and while there is still left, perchance, a little of the precious vintage of former days.

Those visitors, who have penetrated to the innermost sanctum of Professor Smith's office, with its priceless collection of old chemistries and prints and with its scores of framed portraits of chemists looking down from the walls like a cloud of witnesses, know that there is no more fascinating hobby than the pursuit in leisure hours of the cultural side of one's vocation. Professor Smith's object, as modestly stated in his preface, is "to lay before interested readers a hint of the vast stores of early literature relating to chemistry." The book, however, is more than a hint and might almost be termed an anthology, so varied and so interesting are the selections to which the reader's attention is called. Some fifty authors are cited whose published works extend over a period of three centuries, from an edition of Geber printed at Nuremberg in 1545 down to the "Muck Manual" of Samuel L. Dana, printed at Lowell, Massachusetts, in 1842. In addition to ancient works upon alchemy, there are mentioned old treatises, histories, catechisms, conversations, compendia, epitomes, manuals, systems, elements, essays, lectures, dissertations and philosophies of chemistry—a list so general and comprehensive that every chemist, no matter how specialized, will find much to attract his interest. The references to these volumes are enlivened by the sympathetic comments of the author as he opens his treasures before us and calls our attention to this or that passage or illustration. The company to which the reader is admitted is a select one, including not only European celebrities, such as Black, Bergmann, Fourcroy, Lavoisier, Chaptal, Orfila, Parkes, Thomson and Accum, but early American authors such as Rush, Ewell, Macneven, Gorham, Bache, Silliman, Hare and others. The well chosen illustrations of apparatus, title-pages, lecture cards, chemists, etc., lend additional interest to the volume. There are portraits which, once seen, the reader will never forget, such as the cherub face of Boerhaave and the delightful antique of Mrs. Marcet in lace cap and curls. There are also letters, such as the historic message of Lavoisier to Franklin and the charming congratulatory note of John Adams to Gorham which, once read, will stimulate a second and a third perusal.

It is not for correct theories or practical values that we consult the old chemistries which Professor Smith has placed before us, but for a draught of the spirit and enthusiasm with which these works were written. Such, for example, was the glowing zeal of the young Philadelphian, John Pennington, who was stricken by yellow fever in 1793 at the early age of 25, and the title-page of whose "Chemical and Economical Essays" is reproduced in the present volume.

On the first page of his book Professor Smith laments "that in these days of action little patience is had with tales of the past." Posterity, however, will have its revenge for there will be even less of patience a century hence with the chemistries of today. It was Emerson, the wisest of American critics, who wrote that "science must be studied humanly" and it is for the lack of this human element that chemistry is suffering at the present time. The chemists of America may most truly be thankful to Professor Smith that by the single example of this new volume he has refuted the charge of European critics that chemistry in America is wholly industrialized. There are many in this country who believe that chemistry has higher messages than those of industrial benefits—"messages in history, in philosophy, in economics, in social relations, in art, in international relations, in literature and in a wide and extensive culture," to quote from the concluding sentence of Professor Smith's new book. To all chemists, and especially to those who believe in these other messages, the present volume upon "Old Chemistries" is most cordially recommended.

C A BROWNE

Recent Advances in Physical and Inorganic Chemistry. By ALFRED W. STEWART. D.Sc., Professor of Chemistry in the Queen's University of Belfast Fifth edition, Longmans, Green and Company, 55 Fifth Avenue, New York, 1926. xi + 312 pp. 35 figs. 22 × 14 cm. Price \$6 50.

Some seven years have elapsed since the publication of the last (fourth) edition of this book. The author has, therefore, been obliged practically to rewrite it. Only five chapters have survived with minor alterations; twelve new chapters have been added and a corresponding number of chapters in the old edition eliminated. These new chapters deal with hafnium, isobars, the results of mass-spectrography, the segregation of isotopes, the structure of the atom, active hydrogen and nitrogen, some new hydrides, the effect of intense drying and Tesla-luminescence spectra.

These subjects are presented with the same clarity and enthusiasm which characterized the earlier edition. The book represents a useful and valuable digest of the recent progress in the fields which it attempts to cover.

ARTHUR B. LAMB

Physico-Chemical Metamorphosis and Some Problems in Piezochemistry. By ERNST COHEN, University of Utrecht. The George Fisher Baker Non-Resident Lecture-ship in Chemistry at Cornell University. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City, 1926. 190 pp. 58 figs. 23.5×15.5 cm. Price \$2.50.

In the introductory lecture to the series of twenty-one discourses which make up this volume, Professor Cohen quotes from the French savant "Ce n'est pas assez de savoir les principes, il faut savoir manipuler." The book shows that the author has indeed taken this to heart. With charming style and very simply he lays forward and illustrates by examples the principles of polymorphism and some of the problems dealing with the behavior of chemical systems under pressure. At the same time he misses no opportunity of enlarging on those details of experimental technique for which the Laboratory at Utrecht is justly famous. His developments of the electrical methods for investigation of transition points, solubilities, etc., are particularly worthy of notice.

The object of the book may be stated in the author's own words. "It is my purpose to tell you systematically what external conditions of temperature, pressure, solvent, etc., cause the formation of modifications of the same substance and what consequences their existence will have." We think he has succeeded. No one can read the first half of the book without having his ideas of the sanctity of physico-chemical constants and of the nature of matter very salutarily shaken.

The book is easily read and will appeal to all students of physical chemistry; in particular, teachers of the subject should find it very inspiring. Like most series of lectures, however, it deals more with the aspect of the subject as viewed by the author than with the subject as a whole. Hence, its main use to the specialist in the field is as an index to the work of the Utrecht school.

The book is well printed, adequately illustrated and indexed, and the few typographical errors are unimportant.

R. E. GIBSON

Anorganische Chemie. (Inorganic Chemistry.) By Dr. ROBERT SCHWARZ, Professor of Inorganic and Analytical Chemistry at the University, Freiburg. Theodor Steinkopff, Dresden and Leipzig, 1927. xi + 139 pp. 22×15 cm. Price, unbound, M. 8; bound, M. 9.20.

This is a further volume in the series of monographs edited by Dr. Liesegang designed to summarize the progress of research in the various fields of natural science since 1914. Earlier volumes in this series have already presented some features of the progress in inorganic chemistry; for instance, Physical Chemistry, by Benrath; Colloidal Chemistry, by Liesegang; Mineralogical Chemistry, by Eitel; and Atomistics, by Gerlach.

The present volume is particularly concerned with *experimental* inorganic chemistry.

Each element is separately discussed, the order being that of the periodic system. This discussion occupies three quarters of the volume. There are in addition a short chapter devoted to such general topics as the concept of an element, the color of inorganic compounds and the hydrogen compounds of the elements, and another on complex compounds.

In a more convenient form but less complete, this volume covers substantially the same ground as do the "Annual Reports" of the Chemical Society of London in their chapters on Inorganic Chemistry.

ARTHUR B. LAMB

Die Welt der Atome. Zehn gemeinverständliche Vorträge. (The World of Atoms. Ten Popular Lectures.) By Dr. ARTHUR HAAS, Professor of Physics at the University, Vienna. Walter de Gruyter and Company, Berlin, W10, Germany, 1926. xii + 130 pp. 37 figs. 23.5 × 15 cm. Price, unbound, M. 4.80; bound, M. 6.

This book contains, in printed form, a series of lectures delivered to a general audience at the University of Vienna in 1926. The book starts with a short discussion of the Philosophy of Democritus and the first chapter presents some of the general ideas of the atomic theory with the lines of supporting evidence. The structure of electricity and the means of determining the absolute masses of the atoms are clearly discussed. The second chapter discusses the "building stones for atoms." Prout's hypothesis is mentioned and the chapter gives a rapid discussion of cathode rays, alpha-ray tracks, positive-ray analysis and atomic disintegration by alpha-particle bombardment. The following chapters take up in succession "Light Quanta," "Spectra and Energy States," "The Hydrogen Atom," "Elements," "The Atom as a Planetary System," "Molecules," "Radioactivity" and "Transmutation of the Elements."

The author has made a sincere attempt to bring the material included up to date. For example, illinium is included in the list of elements, and the work by Millikan and his co-workers on "stripped atoms" is discussed. The Bohr theory is accepted frankly as the best picture we have of the structure of atoms. The author might be criticized for not stating some of the objections to this theory. In general, the author has included impartially the important pieces of work in the various fields, although the list of workers is necessarily not complete. It might seem somewhat of a mistake not to mention any American contributions in such fields as the determination of the velocity of light, the determinations of the atomic weight of lead from radio-active minerals, the separation of isotopes by diffusion and positive-ray analysis, since other work, frequently not as accurate, is included.

A reader who had had no previous contact with the ideas presented

in the book might find it difficult reading. Any one who has some knowledge of the trend of physics will find the book useful in presenting a connected and logical picture of current ideas. The author has sacrificed rigor for ease of presentation in a few instances but, on the whole, the book is remarkably free from the sort of looseness so frequently encountered in popular treatments of this subject.

W. ALBERT NOYES, JR.

Der Bau der Atome und das periodische System. (The Structure of Atoms and the Periodic System.) By IVAN KOPPEL, Professor at the University, Berlin. Leopold Voss, Leipzig, 1927. vi + 174 pp. 47 figs. 22 5 × 14 5 cm. Price, unbound, M. 9, bound, M. 10.50.

This is a brief attempt to recount and interpret for chemists or for students of chemistry some of the results of modern atomic physics. The author recognizes the necessarily arbitrary nature of the task of selecting material of special importance and interest for chemists, but hopes at least to have removed certain hindrances to the entrance of chemists into this field of study.

Subatomic physics is introduced by a short history of the periodic system, atomic and kinetic theory. The author then lists the principal facts which have led to modern extensions of Dalton's views, and begins his systematic discussion of them with radio-activity. Then follows the action of alpha particles on matter, and the researches on positive rays which have revealed the isotopy of non-radio-active elements and so profoundly influenced our present ideas of the meaning of "an element."

The next chapter deals with x-rays, Moseley's law and the simplified theory of the hydrogen atom as well as the calculation of the constants of Moseley's equation for x-ray emission frequencies. A simple account of "hydrogen-like" spectra introduces the effect of the mass of the nucleus on the motion of the system. In the next chapter the Hamiltonian equations are employed and permit a more general statement of the quantum conditions; then follow elliptical orbits, Stark and Zeemann effects and the relativity mechanics. In the last chapter the reader learns of the speculations of Kossel, Bohr, Stoner and Swinne, concerning the ordering of the non-nuclear electrons. V. M. Goldschmidt's geochemical ideas are mentioned. The treatment follows Sommerfeld in most respects but the material is greatly restricted and simplified. The condensation is excellently done. The reviewer was disappointed not to find more on the nature of non-hydrogen-like spectra, magnetic properties, and also some account of the ion-lattice theory of crystals.

NORRIS F. HALL

Colloids: A Textbook. By H. R. KRUYT, Professor of Physical Chemistry, University of Utrecht. Translated from the Manuscript, by H. S. VAN KLOOSTER, Professor of Physical Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. John Wiley and Sons, Inc., 440 Fourth Avenue, New York City, 1927. xi + 262 pp. 116 figs. 23.5 × 15.5 cm. Price \$3.50.

The author states that his purpose is "to offer a main line of orientation to students who wish to become acquainted with the general trend of colloid chemistry, or who desire to undertake research in this particular branch of chemistry." This purpose has been attained for the most part in so far as his limited space allows. The treatment is divided into four sections; General Methods, Suspensoids, Emulsoids, Special Cases. The treatment of suspensoids is quite the conventional one, although not all of his readers will agree that the dyeing of wool is an example of reversible adsorption and that fastness of dyed fabrics to washing depends upon adsorption equilibrium (p. 38). Langmuir's views on adsorption are questioned on page 28 and adopted on page 103.

In the treatment of emulsoids the author differs sharply from Loeb's ideas. An emulsoid sol consists of particles surrounded by a film of water which protects them against flocculation, chiefly by hydration. The protein emulsoid sols also possess an electrical double layer, one constituent of which originates in the particle itself. The Donnan equilibrium is presented in the usual way and a theory of gelatinizing is presented in considerable detail. Soaps are considered as colloids intermediate between suspensoids and emulsoids. McBain's theory of the ionic micelle is considered superfluous. The colloidal soap particle consists probably of salt molecules, only those on the outside being ionized and taking part in the electrical double layer.

The translator deserves the highest commendation for his skill in rendering a foreign language into English. This task has been accomplished with the complete elimination of foreign idiom, so that the text as presented reads as if it were originally written in English.

F. B. MILLARD

Einführung in die Chemie der Polymeren Kohlenhydrate: Ein Grundriss der Chemie, der Stärke, des Glykogens, der Zellulose und anderer Polysaccharide. (Introduction to the Chemistry of Polymeric Carbohydrates: An Outline of the Chemistry of Starches, Glycogens, Cellulose and other Polysaccharides.) By P. KARRER, Professor at the University, Zürich. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1925. ix + 285 pp. 21.5 × 15 cm. Price, bound, 16 Mk.; unbound, 13 Mk.

In this treatise the author gives a critical review of recent work on the chemistry of starch, glycogen, cellulose and related polysaccharides.

The seven chapters comprise (1) starch, (2) glycogen, (3) lichenin, (4) cellulose, (5) inulin, (6) chitin and (7) other polysaccharides (pentosans, hexosans).

The topics are treated throughout from the physico-colloidal standpoint, and views of other workers are reviewed critically and impartially.

The author's valuable personal contributions to this field are well known and it is this intimate, personal contact which has enabled him to portray with remarkable clarity and originality the properties of these natural compounds and the intimate relationship existing between them.

The volume can be heartily recommended to all workers in the field of polysaccharide chemistry.

HAROLD HIBBERT

Problems in Organic Chemistry. By H. W. UNDERWOOD, JR., Ph. D., Instructor in Organic Chemistry, Massachusetts Institute of Technology. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1926. x + 233 pp. 21 × 14 cm. Price, \$2.00.

Far too large a part of the instruction in science in our colleges and universities consists in filling the minds of students with facts which they are expected to remember. It is much more important that they should be taught to use the facts at their command and the knowledge available in textbooks and handbooks in a constructive way. This is particularly true of organic chemistry. The facts of the science are almost unlimited in number and the most conscientious student can retain only a few in his memory. As our author well says, "Descriptive questions which involve merely a restatement of the material in textbooks or lecture notes have little or no value in teaching students how to master the principles of the subject and apply them to concrete cases."

Dr. Underwood's book is well adapted to remedy this defect in the ordinary teaching of organic chemistry. In each of the twenty-four chapters after the first two a brief statement is given about the characteristics and nomenclature of some class of organic compounds and, in nearly all, there are charts showing the most important relations to other classes of compounds. Then follow numbered paragraphs, each containing from one to eight or ten problems or questions. The distinction between problems which the student should be able to solve from his knowledge of the subject and questions which involve detailed knowledge to be found in textbooks or handbooks is not kept as clear as it might have been and some of the paragraphs resemble a quiz-compend rather than genuine problems. The design of the book is certainly very excellent and it will prove very useful both to students and teachers.

The question might be raised, of course, whether such problems would not find their place better in a comprehensive textbook of organic chemistry but so long as the textbooks in common use do not provide such problems, such a book is timely.

In reading the discussions of nomenclature, one is impressed with the chaotic state of the subject and it would have been well if the author

had paid closer attention to the principles followed by *Chemical Abstracts*, the best authority we have in English. Nomenclature is, after all, a matter for authority and not for the exercise of personal idiosyncracies.

It may not be out of place to remark that the exact atomic weight of carbon, 12.005, is quite unnecessary in calculating the analyses of organic compounds. The factor 3/11 for the carbon of carbon dioxide is sufficiently accurate even for very accurate determinations. Even the value 1.008 is scarcely necessary for hydrogen. If 1 is taken for hydrogen and 1/9 of the weight of water found is taken as the weight of the hydrogen found, two errors which very nearly compensate each other are introduced and the results are well within the errors of ordinary analyses.

W. A. NOYES

A Text-Book of Organic Chemistry. Historical, Structural and Economic. By JOHN READ, Professor of Chemistry, University of St Andrews G Bell and Sons, Ltd, London, 1926. xii + 680 pp 87 figs 19.5 × 13 cm Price, 12s 6d net.

"The treatment of the subject has been stripped of a good deal of detail which is often included in a preliminary account, but which is here replaced by other matter illustrating in broad outline the scope of organic chemistry, its position as a link between physical and biological science and its industrial and economic interest. In accordance with the same principle, the chemistry of the fats, carbohydrates, proteins and other important natural groups has received an unusual prominence in the scheme of presentation. These readjustments of emphasis have been effected with little compunction, in the belief that a beginner in organic chemistry should be encouraged to utilize his available time and energy in obtaining a comprehensive view of the science and in absorbing its spirit and general principles, rather than in 'learning' lists of specialized reactions and inter-relationships."

The reviewer has had the book on his desk an inordinate time—certainly long enough to give it a very thorough reading. All of the book has not been read. However, enough of it has been read to warrant the following observations. It is an excellent book, one of the best of its kind; it is unusually free from typographical errors, and the format is good.

Undoubtedly many in this country will object to giving the first 60 pages to an historical development of chemistry. Few will deny that these early chapters are interestingly presented. The author in his preface makes a good pedagogical case for the inclusion of the historical matter. It is not an overly serious matter if all the students do not read all of the historical development at this stage of their training. There would still be left a large number of pages of excellent material.

HENRY GILMAN

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THE POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE

BY ROSCOE H. GERKE AND M. DOROTHY ROURKE

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The original purpose of this investigation was to study the properties of the gold-aurous oxide electrode. The authors, however, were entirely unsuccessful in preparing aurous oxide by duplicating the methods described in the literature or by any other methods which suggested themselves. During the course of the investigation it was observed that the potential of the gold-auric oxide electrode was about the same as that reported in the literature for the gold-aurous oxide electrode.¹ Hence, it is the purpose of this paper to present the results of the experiments on the gold-auric oxide electrode and to present briefly the experimental facts which lead to the conclusion that it is doubtful whether aurous oxide has ever been prepared.

The Gold-Auric Oxide Electrode

The cell, $\text{Hg(l)}, \text{Hg}_2\text{SO}_4(\text{s}), \text{H}_2\text{SO}_4, \text{Au}_2\text{O}_3(\text{s}), \text{Au (cryst.)}$ was employed in the measurement of the potential of the gold-auric oxide electrode. The cell consisted of two half-cells² with side arms dipping into a small beaker containing sulfuric acid of the same concentration as in the half-cells. Thus, the cell contained no liquid potential. The electromotive force measurements were made with a Leeds and Northrup student potentiometer and galvanometer at room temperature, which was about 25° . With this apparatus the electromotive force could be read easily to a millivolt, which is sufficiently precise for cells containing gold electrodes.

The auric oxide was prepared by the method of Krüss.³ The gold was

¹ Campbell, *Chem. News*, **96**, 257 (1907).

² Sherrill, "Laboratory Experiments on Physico-Chemical Principles," The Macmillan Company, 1923.

³ Krüss, *Ann.*, **237**, 291 (1887).

precipitated by the reduction of auric chloride solution with sulfur dioxide solution. The gold appeared as thin crystals. The gold-auric oxide half-cell was constructed in the following manner. The gold crystals mixed with an equal amount of auric oxide in sulfuric acid solution were introduced into the electrode vessel. A dip electrode consisting of a glass tube with a platinum wire sealed through the end made electrical contact with the gold. The results on cells with three concentrations of sulfuric acid are given in Table I.

TABLE I		
POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE AT 25°C.		
Concn., H ₂ SO ₄	Volts	Volts
0.0506	0.599 ± 0.002	1.353 ± 0.002
1.031	0.629 ± .002	1.367 ± .002
1.031	0.690 ± .001	1.365 ± .002

The electromotive force of the cells increased for about 24 hours and after that time it was constant within the limits given in Table I, Col. 2, whether the cells were agitated or not. The first column in Table I gives the concentration of the sulfuric acid in formula weights per 1000 g. of water. Cols. 2 and 3 are, respectively, the electromotive force of the cells, Hg(l), Hg₂SO₄(s), H₂SO₄, Au₂O₃(s), Au (cryst.) and H₂ (1 atm.), H₂SO₄, Au₂O₃(s), Au (cryst.). The values for the electromotive force⁴ of the latter cell were calculated from the observed values in Col. 2, and from values of the electromotive force of the cell, H₂ (1 atm.), H₂SO₄, Hg₂SO₄(s) Hg.⁵

From the average of the values in Col. 3, the potential of the gold-auric oxide electrode, Au (cryst.), Au₂O₃(s) H⁺ is -1.362 volts, which is somewhat larger than Campbell's value, of about -1.2 volts for the gold-aurous oxide electrode, Au, Au₂O(s), H⁺. This latter value is corrected neither for liquid-junction potential nor by activity coefficients.

The value 18,810 cal. for the free energy of formation of auric oxide has been computed from the electromotive force of the cell in Col. 3 for the change of state, 3H₂ + Au₂O₃(s) = 2Au (cryst.) + 3H₂O(l). The dissociation pressure, 1.46 × 10⁹ atmospheres shows that auric oxide is very unstable with respect to the elements at room temperatures.

Aurous Oxide

There is no *a priori* reason why aurous oxide can or cannot be made. The necessary conditions for its preparation are: (1) a chemical reaction with a negative free energy increase and (2) the rate of decomposition of the substance, once prepared must be slow.

The methods which were employed to prepare aurous oxide will be

⁴ The conventions as to sign of electromotive force are the same as those of Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

⁵ Randall and Cushman, *THIS JOURNAL*, **40**, 393 (1918).

mentioned very briefly. The investigators who report analyses of their product are Figuier⁶ and Krüss.⁷ Both of these methods of preparation were tried. Both preparations had the appearance given in the descriptions, but the microscope revealed the presence of metallic gold. The method used by Campbell¹ was tried with the same results. Furthermore, the boiling of auric chloride with potassium hydroxide solution, the direct reduction of auric oxide by sulfur dioxide solution, and the treatment of aurous iodide with acids and bases did not give a product which was free from metallic gold.

In addition, Hartung⁸ has made a very thorough study of methods of preparation of aurous oxide. He observed that chemical analysis is not sufficient evidence to prove whether a given preparation is aurous oxide or not. He found that his preparations contained metallic gold and concluded that "No evidence has therefore been obtained to show that aurous oxide exists; its chemical and physical properties are those of a mixture of gold and auric hydroxide."

Finally, Buehrer⁹ made a preparation by a method adapted from that of Krüss,⁷ which was employed with crystalline gold as a gold-gold oxide electrode. This electrode when compared with a hydrogen electrode in sulfuric acid solution gave an initial value of about +1.1 volts. After two years the electromotive force had increased to +1.363 volts. This result can be interpreted in two ways; one in which it is assumed that aurous oxide is thermodynamically more stable than auric oxide, in which case the electrode initially consisted of Au (crystalline), Au₂O (solid), H⁺; and second, which the present writers have suggested, in which it is assumed that aurous oxide did not exist in the blue-black precipitate in the electrode and that the electrode consisted initially of Au (colloidal), Au₂O₃ (solid), H⁺. If the colloidal gold slowly changed to crystalline gold, the electromotive force would increase to the value 1.363 volts. The latter assumption has in its favor the fact that the blue-black precipitate has somewhat the color of the purple of Cassius, which is characteristic of colloidal gold.

In conclusion, it may be said with confidence that it is doubtful whether a pure preparation of aurous oxide has ever been prepared.

Summary

1. The potential of the gold-auric oxide electrode, Au (cryst.), Au₂O₃ (s), H⁺ has been found to be -1.362 volts.
2. The free energy of formation of auric oxide at 25° has been found to be +18,810 cal. from electromotive-force measurements.

⁶ Figuier, *Ann. chem. phys.*, **11**, 339 (1844).

⁷ Ref. 3, p. 279.

⁸ Hartung, *J. Chem. Soc.*, **129**, 1349 (1926).

⁹ Buehrer, Wartman and Nugent, *THIS JOURNAL*, **49**, 1271 (1927).

3. It is shown that it is doubtful if a pure preparation of aurous oxide has ever been prepared.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICS AND OF PHYSICAL CHEMISTRY
OF THE UNIVERSITY OF MISSOURI]

LUMINESCENCE OF GRIGNARD COMPOUNDS IN ELECTRIC AND MAGNETIC FIELDS, AND RELATED ELECTRICAL PHENOMENA

BY R. T. DUFFORD, DOROTHY NIGHTINGALE AND L. W. GADDUM

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Previous work by the authors and their colleagues¹ has shown the existence of interesting and remarkable regularities in the relations between chemical structure and the brightness and spectral distribution of the light emitted when ether solutions of Grignard compounds, having the general formula $RMgX$, are oxidized with air or oxygen. The behavior of this group of compounds raises many questions regarding the molecular structures involved.

It seemed possible that some light in this direction might be obtained from experiments with strong magnetic and electric fields. If the radiators are electrons in orbits, as current ideas go, it seemed barely possible that the application of a strong field might bring about a uniform orientation of the molecules, or of the orbits within the molecules, and that this condition might result in polarization of the light emitted in such a field.

The experiment was therefore made of oxidizing certain of the brighter compounds in magnetic fields of about 15,000 gauss; but in every case, polarization appeared to be completely lacking. If it existed, it could not have exceeded one or two per cent. However, one effect was clearly visible; in the strongest fields, there was a distinct tendency for the most of the emission to occur in the most intense parts of the field, near the pole pieces. Immediately on applying the field, a streaming appeared in the solution, with the brightening at the sides of the crucible containing the solution. It appeared as if the effect were mechanical, either the Grignard or, more probably, the oxidation product, being sufficiently paramagnetic to be drawn to the poles. If the solution were very clear to begin with, it would soon show minute black specks being drawn to the poles with the streams. Most of the oxidation product collected near the poles. The effect is shown well by $p\text{-BrC}_6\text{H}_4\text{MgBr}$. It does not, however, appear in weak fields.

¹ Dufford and co-workers, *THIS JOURNAL*, 47, 95 (1925); 45, 2058 (1923); 45, 278 (1923); *J. Optical Soc. Am.*, 9, 405 (1924); *Phys. Rev.*, 21, 203 (1923); 27, 247 (1926).

The similar study of these compounds in strong electric fields is impossible, because of the remarkably high conductivity of their solutions which are, indeed, quite comparable with aqueous solutions in showing the properties of electrolytes.² Tests were made with voltages up to 1500. The experiments at once brought out what appears to be a quite distinct type of luminescence, which occurs at one or both electrodes, and is not due to oxidation at the surface of the liquid. Usually the light appears at the anode but sometimes it is at the cathode, or at both electrodes. The effect is not always visible at low voltages. A surprising fact is that the brightness of the light appears to have little if anything to do with the brightness obtained on reaction with oxygen. In no case was any trace of polarization observed in the light. Table I gives a list of typical examples and it will be noted that some compounds that give no light on oxidation with oxygen show the effect, while the brightest of the oxy-luminescent substances hardly show the present effect at all.

TABLE I

LUMINESCENCE DURING ELECTROLYSIS OF GRIGNARD COMPOUNDS

Grignard compound from	Light during electrolysis	Remarks
Methyl iodide	None	
Ethyl iodide	None	
<i>n</i> -Butyl bromide	None	
<i>iso</i> -Amyl bromide	None	
<i>n</i> -Lauryl bromide	Faint	Seen only above 1000 v.
Trimethylene bromide	Faint	Seen only above 500 v.
Bromocyclohexane	Faint, momentary	Seen only above 1000 v.
Benzyl chloride	None	
β -Bromostyrene	Faint	Less than with oxygen
Phenyl bromide	Fair	About equal to light with O ₂ ; easily visible at 110 v.
Phenyl iodide	Faint	Visible with 110 v.
<i>p</i> -Iodotoluene	Fair	Stronger at 1500 v. than oxidation
<i>p</i> -Chloro-bromobenzene	Very faint	Much less than with O ₂ even at 1500 v.
<i>p</i> -Dibromobenzene	Faint	Less than with oxygen
1,2,4-Chloro-bromotoluene	Faint	Visible above about 500 v.
α -Bromonaphthalene	Very faint	
β -Bromonaphthalene	Faint	At cathode
1,4-Chloro-bromonaphthalene	Fair	At anode; appears between 500 and 600 v.
	Faint	At cathode; appears between 600 and 700 v.
β -Iodonaphthalene	None	

In a recent article, Evans and Diepenhorst³ have questioned the conclusion of the writers that luminescence on oxidation of a Grignard com-

² Nelson and Evans, *THIS JOURNAL*, 39, 82 (1917). Kondyrew, *Ber.*, 58, 459 (1925).

³ Evans and Diepenhorst, *THIS JOURNAL*, 48, 715 (1926).

pound with oxygen, in ethyl ether solution, appears only if the —MgX group is attached directly to an unsaturated carbon atom. They state that they have obtained light from several Grignard compounds made from derivatives of saturated hydrocarbons, but do not state what solvent was used or whether the light was obtained from the crystallized compounds. The writers have carefully re-examined every such compound mentioned by Evans and Diepenhorst, without finding light in any case. Evidently the conditions for obtaining light, if it is emitted by such compounds, were not the same as used by the writers, that is, combination with oxygen while dissolved in ethyl ether.

Regarding the brightness of these compounds, Evans and Diepenhorst state that the "luminescence is proportional to the molecular weight of the halogen derivative so long as a definite series is considered without change in the chemical nature of the group or—in the case of the aromatic compounds—in position." So far as aliphatic compounds are concerned, Evans and Diepenhorst themselves appear to disprove the statement, by tabulating lauryl bromide as fainter than *iso*-amyl bromide. In the entire absence of quantitative measurements of brightness, the statement that a *proportionality* exists seems hardly justified. In the case of the aromatic compounds, it is true that the brightness increases when aliphatic groups of increasing formula-weight are substituted in the benzene ring, but this is the only case in which the brightness has been clearly shown to increase with molecular weight. On the other hand, there are several series, probably just as fairly called chemically similar, in which the brightness decreases when the molecular weight increases. This is the case in marked degree with the series $\text{C}_6\text{H}_5\text{MgCl}$, $\text{C}_6\text{H}_5\text{MgBr}$, $\text{C}_6\text{H}_5\text{MgI}$, with the series *p*- $\text{ClC}_6\text{H}_4\text{MgCl}$, *p*- $\text{BrC}_6\text{H}_4\text{MgBr}$, *p*- $\text{IC}_6\text{H}_4\text{MgI}$, and the series *p*- $\text{ClC}_6\text{H}_4\text{MgBr}$, *p*- $\text{BrC}_6\text{H}_4\text{MgBr}$, *p*- $\text{IC}_6\text{H}_4\text{MgBr}$. Other similar series are known. Evans and Diepenhorst have criticized the writers for concluding that mass is not the controlling factor, and that its influence is small compared with effects connected with the chemical nature of the compounds; but in view of the fact that only one series of compounds behaves in the way demanded by the "proportionality" of Evans and Diepenhorst, while there are several series which do not, and many more compounds which do differ chemically (for example, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{MgBr}$) and which, when compared in molecular weight, seem to vary in brightness without much regard to molecular weight, the present writers feel that the effect of mass, if any, has not been clearly demonstrated. The question is simply one of interpretation of results, for with all these aromatic compounds the observations of Evans and Diepenhorst appear to repeat closely those of the writers.

The same authors criticize the writers for not noticing that the positions of the bands in the spectra from the oxidation of *p*- $\text{ClC}_6\text{H}_4\text{MgBr}$ and *p*- $\text{BrC}_6\text{H}_4\text{MgBr}$ are identical. They admit, however, that the light in

the two cases differs in color. They attempt to explain the difference by saying that the light must be a mixture of fluorescence and chemiluminescence. The explanation is both untenable and unnecessary. In all known cases, the ratio between the intensities of fluorescent and of exciting light is so small that it is almost inconceivable that light as faint as chemiluminescence could produce perceptible fluorescence, and if it did, the spectra would show it, for the fluorescence spectra that would be observed are multiple-banded, and these bands do not appear on the photographs; they would be readily distinguishable if present. However, difference in color can mean only one thing—a difference in spectral distribution of energy; this is true no matter what the origin of the light may be. Now each of the chemiluminescence spectra shows a single, fairly symmetrical band, and the bands do not differ greatly in width. About the only possible difference would thus appear to be in the location of the maxima. Even a rough examination of the spectra, either in the articles by the writers or in those of Evans and Diepenhorst, will show that the maximum for $p\text{-BrC}_6\text{H}_4\text{MgBr}$ lies somewhat on the violet side of the helium line at $\lambda 4472$, while for $p\text{-ClC}_6\text{H}_4\text{MgBr}$ the maximum lies considerably on the long wave-length side of this line. The existence of such a difference was of course clearly indicated by the earlier work in which monochromatic filters were used.

The processes involved in the luminescence during electrolysis are probably different from those occurring during combination with oxygen. It is, therefore, not necessary to conclude that since one process gives luminescence, the other must also. The fact that the processes are different is shown by the following. It is found that while some Grignard compounds on electrolysis deposit magnesium immediately, others do not at first; the deposition potential of the magnesium varies for the different compounds, in some cases being high enough for other reactions to occur first. In such cases, it is often observed that a brown, oily liquid forms, which settles slowly. Some of this material seems to form in some cases even when magnesium is deposited. The liquid appears to be $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$. This substance can be prepared by methods not involving the use of Grignard compounds. However it is prepared, it is found to have the property of emitting light on electrolysis, just as many of the Grignard compounds do. The light emitted is so similar in the two cases that it seems probable that in many instances, especially with the saturated compounds, the formation of this substance, or possibly other etherates, may explain the entire luminescent effect.

Incidentally, it is worth pointing out that the magnesium which is deposited by electrolysis of these compounds is in a highly active state; it can be used to obtain good yields of some compounds, as $\text{C}_6\text{H}_5\text{MgCl}$, that are not easy to make.

The fact that ether solutions of Grignard compounds are closely comparable in their electrolytic properties with aqueous solutions of inorganic substances, opens a wide field for investigation. Some progress has been made by the writers and their colleagues in three directions: the study of decomposition potentials, the study of the complicated processes occurring in the electrolysis of these compounds, and the study of electrode potentials. The present article, however, will present only some important preliminary results from the last of these fields, that have shown a most interesting effect which is a converse of the luminescence on electrolysis. It is hoped that further results may be presented in later papers.

If a pair of strips of dissimilar metals is carefully cleaned and immersed in a solution of a Grignard compound, the strips will be found to have different potentials; they are the electrodes of a cell, a battery. Of course the cell must be sealed to prevent oxidation of the solution. A number of such cells have been studied, using a potentiometer outfit capable of measuring e.m.f.'s to 0.00005 volt.

The e.m.f. of such a cell varies greatly, for three reasons: (1) the cells have high temperature coefficients; (2) they are strikingly sensitive to changes in the illumination they receive; (3) the e.m.f. may be a periodic function of the time, depending somewhat on the previous history of the cell. These facts make it extremely difficult to obtain results which are quantitative and reproducible and the following results are therefore regarded as only preliminary.

The luminescence, during electrolysis, having suggested the possibility of a converse effect, it did not take long to trace certain violent eccentricity in the behavior of the first such cell studied, to the flashing on and off of the thermostat lamp in the water-bath used for regulating the temperature of the cell. The cell was put in a light-proof box, in a liter beaker of water kept at $21^{\circ} \pm 0.1^{\circ}$. The mere opening of a shutter in the box, exposing the cell to the light from a 100-watt incandescent lamp a meter away, would instantly raise the voltage of the cell to several times its value in the dark. The incandescent lamp was kept running continuously. An experiment with colored water in the beaker indicated that red light was not the most effective, but the use of glass containers means that the effective light is either visible or near ultraviolet. Both aliphatic and aromatic Grignard cells show the effect.

Fig. 1 shows the effect of *continued* irradiation on a cell with gold and silver electrodes, in molal solution of phenylmagnesium bromide. The cell was kept in the dark until the e.m.f. was steady. On opening the window to the light from a mercury arc, a constant source, the e.m.f. is seen to rise suddenly, to oscillate about a final value, and finally to become steady after about four hours. As readings were made at short intervals, even one minute apart at the critical parts of the curve, the

effect is not the result of accidental variations of a few readings. The second irradiation shows the same effect less prominently; also the less sudden drop in voltage when the light was excluded. Succeeding irradiations produced smaller effects, as shown. The temperature was constant to 0.05° in these experiments.

Other similar cells have given various similar curves (a number of these were shown at the Tulsa meeting of the American Chemical Society), some having a much greater oscillation in the e.m.f., and some showing the oscillations damped more quickly, some less quickly, than the example

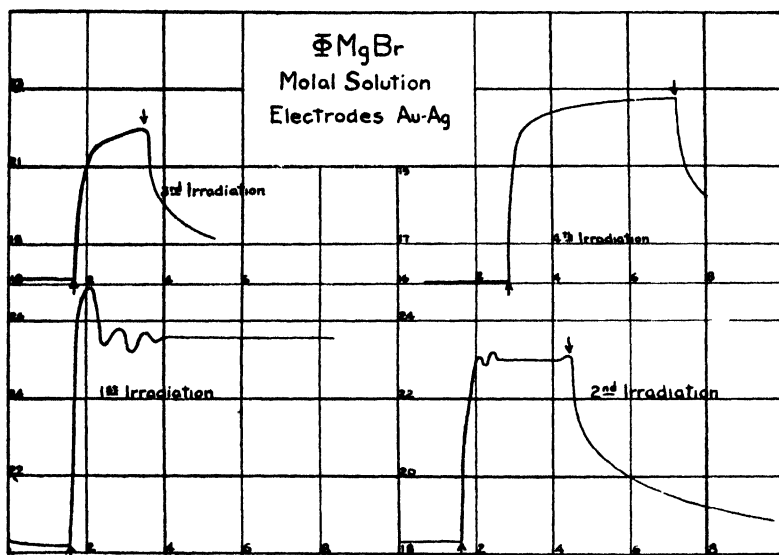


Fig. 1.

shown, but all showing the marked sensitivity to light. Similar oscillations were observed in deposition potentials taken with platinum electrodes. The work of Hedges⁴ and associates indicates that such periodic functions of time may frequently be found in electrolysis of aqueous solutions of metal salts. No general theory of this effect has been given.

Cells with lead and copper electrodes gave erratic results, probably due to reactions at the electrodes; on standing, an oily liquid drips from the electrodes, and the solution shows a qualitative test for copper. While the values of the e.m.f. are not reproducible, the sensitivity to light appears to be always present, and the curves showing voltage variation with time have the same general shape. Magnesium-zinc cells, also sensitive, give much more closely reproducible e.m.f.'s.

Using a flowing junction method, with a cell made up of $\text{Mg} \mid \text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ (Sat. sol.) $\mid \text{C}_2\text{H}_5\text{MgBr}$ (1.5 M) $\mid \text{Mg}$, e.m.f.'s are obtained

⁴ Hedges, *J. Chem. Soc.*, 127, 1013 (1925).

which are very steady and reproducible, readings checking repeatedly within one or two in the third significant figure. The cell used gave about 0.2 volt, but the numerical value is significant only in showing the order of magnitude of the effect measured, since the exact value of the concentration of the Grignard solution was not known.

Summary

1. It is shown that strong magnetic fields produce no polarization in the light from the oxy-luminescence of ether solutions of Grignard compounds, but may affect the brightness.

2. The application of electric fields often causes an unpolarized luminescence at one or both electrodes, accompanying the electrolysis of the solution. The process involved appears to be quite distinct from the oxy-luminescence.

3. Preliminary study of electrode potentials in cells containing ether solutions of Grignard compounds shows that the voltage of such cells is very sensitive to light and that, following a change in illumination, the voltage may be a periodic function of the time.

4. Using a flowing-junction method, closely reproducible voltages were observed.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A THERMODYNAMIC TREATMENT OF CERTAIN MAGNETIC EFFECTS. A PROPOSED METHOD OF PRODUCING TEMPERATURES CONSIDERABLY BELOW 1° ABSOLUTE

BY W. F. GIAUQUE

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Some years ago the author's interest in cryogenic work led to a consideration of possible substitutes for the commonly used methods of producing low temperatures.

While a method of producing very low temperatures was devised, the lack of necessary facilities has caused a temporary delay in the actual experiment and it is desired to transmit the underlying ideas at this time.

The reversible transfer of heat from one temperature to another requires a working substance which is capable of undergoing an isothermal entropy change at the temperatures concerned.

From a practical standpoint, this entropy change must be considerable in view of the unavailability of those theoretically convenient, thermally non-conducting materials.

Compared to those of pressure, the effects ordinarily produced by obtainable electric and magnetic fields on the neutral states of matter are minute. However, a critical consideration indicated that while the latter

cannot compete with pressure in producing a change in entropy at ordinary temperatures, a magnetic field will produce large effects at very low temperatures.

The important point is that the magnetic effects are large when pressure is no longer practicable as a means of producing a further drop in temperature.*

Before considering the available experimental data which lead to this conclusion it will be desirable to collect or derive certain thermodynamic formulas. Where possible the nomenclature of Lewis and Randall will be adopted.¹

The second law of thermodynamics as applied to substances in magnetic fields is $\oint dI + T dS = dE + PdV$.² Keesom omitted the PdV term, which actually makes but small difference. $\oint dI$ = the magnetic work done on the substance; $T dS$ = temperature times entropy change = the heat added; dE = the increase in internal energy; PdV = the work done against an external pressure; I = the intensity of magnetization in excess of that which would be in the same space if unoccupied by matter; $\chi = I/\oint =$ the molal susceptibility.

Since the method commonly used in the determination of magnetic properties involves the maintenance, as nearly as possible, of a constant magnetic potential, and also since we believe that the transfer of material from one maintained potential to another is somewhat easier to visualize than is an integral potential effect, we shall adopt the former viewpoint.

It will be convenient to extend the definition of heat content from $II = E + PV$ to $II = E + PV - \oint I$. The $\oint I$ term is included for a reason entirely analogous to that leading to the inclusion of the PV term. This latter is convenient, due to the maintenance of constant pressure by the earth's atmosphere under ordinary conditions.

Then as usual we may write the free energy as $F = II - TS$, $dF = dII - T dS - S dT = V dP - I d\oint - S dT$. Thus, at constant T and P ,

* Since this paper was submitted for publication there has appeared in the *Annalen der Physik* 81, 1154 (1926) a paper by P. Debye, who has independently arrived at the idea of utilizing the magnetic properties of $Gd_2(SO_4)_3 \cdot 8H_2O$ for refrigeration. Although the author of the present paper has frequently discussed his proposed method with numerous colleagues since 1924, the idea was not otherwise announced until the April 9th 1926 meeting of the California Section of the American Chemical Society when Professor W. M. Latimer discussed this author's proposed use of $Gd_2(SO_4)_3 \cdot 8H_2O$ for obtaining temperatures considerably below 1°K. Since the conception of the idea, equipment for producing liquid hydrogen in the necessary amount has been constructed and placed in operation. A helium liquefaction cycle which should soon enable experimental verification is now in process of construction.

¹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

² Keesom, *Comm. Phys. Lab. Leiden*, Suppl. No. 32a; Keesom (with note by H. A. Lorentz), *ibid.*, Suppl. No. 32b.

$dF = -Id\mathfrak{H}$ and the work done by a mole of substance when it is reversibly drawn into a field $= -\Delta F = \int_1^{H_2} Id\mathfrak{H}$.

Experimentally,³ consider the material investigated to be in the form of a cylinder of sufficient length to extend from the uniform field between the pole pieces of a magnet, through the magnetic gradient to a position where the field is negligible. When the cylinder moves into the field the net result has been a transfer of material from $\mathfrak{H}_1 = 0$ to \mathfrak{H}_2 . The force times the distance necessary to move one mole into the field H_2 is equal to $-\Delta F$.

$(\partial\Delta F/\partial T)_{\mathfrak{H},P} = -\Delta S$, and $-T\Delta S$ is the heat given out during the isothermal magnetization.

When values of susceptibility are given, an alternative method is as follows: $TdS = dE + PdV - \mathfrak{H}dI = dII + Id\mathfrak{H} - VdP$, from which

$$(\partial S/\partial \mathfrak{H})_{P,T} = (\partial I/\partial T)_{P,\mathfrak{H}} = \mathfrak{H}(\partial \chi/\partial T)_{P,\mathfrak{H}} \text{ and } \Delta S = \int_{\mathfrak{H}_1}^{\mathfrak{H}_2} (\partial I/\partial T)_{P,\mathfrak{H}} d\mathfrak{H}.$$

Diamagnetism is practically independent of temperature and thus there is nearly zero heat effect when a diamagnetic substance is introduced into a field.

The ideal paramagnetic substance follows the well-known law $\chi T = C = \text{constant}$, proposed by Curie⁴ and first explained by Langevin.⁵

For such a substance, $\Delta S = -\mathfrak{H}^2 C/2T^2$ when it is taken from zero field to field \mathfrak{H} . The inverse square proportionality of temperature to ΔS leads to considerable effects at very low temperatures, as will be shown later. The above expression for ΔS would lead to infinite decrease in entropy during magnetization at the absolute zero, which conflicts with the accepted view of the finiteness of entropy.⁶ The explanation, as in other such cases, is furnished by quantum mechanics and the fact that Curie's law is a limiting case for $\mathfrak{H} = 0$.

The low-temperature experimental data⁷ on gadolinium sulfate, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, so satisfactorily illustrate the possibilities that they alone will be considered.

Table I gives the values of the Curie constant at various temperatures for one gram atom of gadolinium as the hydrated sulfate. The various experiments have been carried out on two different tubes of material known as Gd I and Gd II.

³ Gouy, *Compt. rend.*, 109, 935 (1889). Onnes and Perrier, *Comm. Phys. Lab. Leiden*, Suppl. No. 139a.

⁴ Curie, *J. phys.*, 4, 197 (1895).

⁵ Langevin, *Compt. rend.*, 140, 1171 (1905).

⁶ The relation of this entropy change to our viewpoint on the third law of thermodynamics will be considered in the following article [Giauque, *THIS JOURNAL*, 49, 1870 (1927)].

⁷ (a) Onnes and Perrier, *Comm. Phys. Lab. Leiden*, No. 122a. (b) Onnes and Oosterhuis, *ibid.*, No. 129b. (c) Onnes, *ibid.*, No. 140d. (d) Woltjer, *ibid.*, No. 167b. (e) Woltjer and Onnes, *ibid.*, No. 167c.

TABLE I
CURIE CONSTANT OF $Gd_2(SO_4)_3 \cdot 8H_2O$ PER GRAM ATOM OF Gd

T	χT	Tube	Observer	T	χT	Tube	Observer
290.3	7.80	Gd I	O. and P.	14.68	8.04	Gd I	W.
20 33	7.89	Gd I	O. and P.	293.1	7.54	Gd II	O. and O.
17.01	7 81	Gd I	O. and P.	20.1	7.49	Gd II	O. and O.
13 91	7 64	Gd I	O. and P.	20.42	7.59	Gd II	W.
20 31	8 01	Gd I	W.	13.98	7.57	Gd II	W.

O. and P., Onnes and Perrier, W., Woltjer; O. and O., Onnes and Oosterhuis.

The perfection of the magnetic behavior is clearly demonstrated. The constancy during a given series of measurements exceeds the agreement between the various series by a considerable amount, thus indicating constant error in a given set. For example, it is pointed out by Woltjer that the Gd I tube was out of center during his measurements.

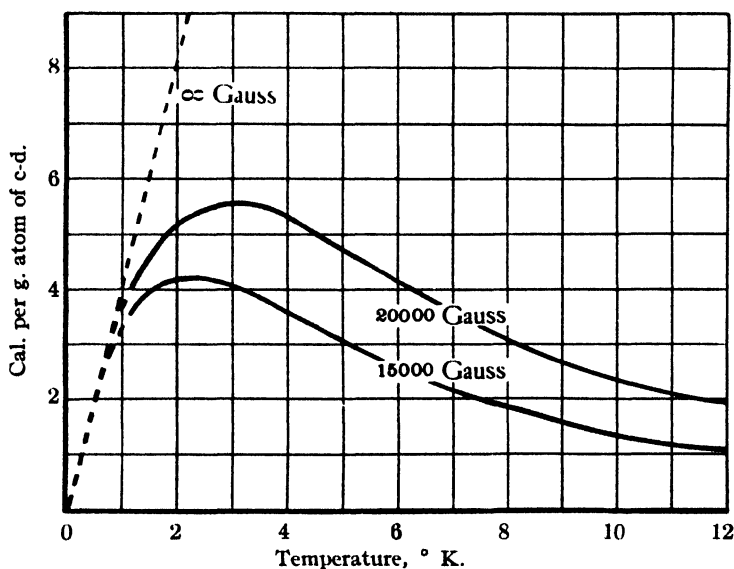


Fig. 1.

Measurements have also been carried out by Woltjer and Onnes^{7c} at various temperatures from 1.3°K. to 4.2°K. with continued perfect behavior except deviations due to approaching saturation. These latter measurements have been considered in some detail in the following paper. From them we have calculated by graphical integration the values of ΔF for magnetization. The temperature coefficient of ΔF gives ΔS for the process and $-T\Delta S$ the heat given out during isothermal magnetization. At 1.3°K. a field of 20,000 gauss produces a decrease in entropy of 3.3 cal. per degree per gram atom of gadolinium. The decrease for 15,000 gauss is 2.9 cal. per degree at the same temperature. The heat evolved

during magnetization by fields of 15,000 and 20,000 gauss is plotted against temperature in Fig. 1. While the amount of heat is small, the effects are actually large when the temperature at which they occur is considered. For purposes of comparison it may be noted that an entropy change of 3.3 cal. per degree at room temperature corresponds to about 1000 cal.

It is apparent that a Carnot cycle could be used to transfer heat from one temperature to another. However, we believe that the following somewhat simpler procedure would suffice to produce temperatures much lower than those produced by any present method. (1) Magnetization of the working substance while it is in thermal contact through gaseous conduction with liquid helium preferably boiling at reduced pressure. (2) Demagnetization after the space between the working substance and the liquid helium bath has been evacuated.

Dysprosium sulfate, $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, or some other "diluted" dysprosium or holmium compound would apparently be the best working substance obtainable, the reason for this being that measurements indicate that dysprosium and holmium have about 10/7 the magnetic moment possessed by gadolinium. The "dilution" of the magnetic atoms by means of non-magnetic atoms appears to be necessary if perfect magnetic behavior is to be expected. This question has been discussed by Onnes and Oosterhuis.⁸

It does not appear probable that $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ would have any considerable heat capacity in the region about 1°K., but no heat-capacity data are available to decide this point. We expect to investigate the heat capacity of substances of this type at very low temperatures in the near future.

The very reversible character of the process is indicated by the absence of hysteresis effects. Breit and Onnes⁹ have investigated the hysteresis of chromic chloride and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ at the boiling point of hydrogen and very high frequencies, and while the susceptibility of both materials was apparently lowered they concluded that "The order of magnitude of the susceptibility is unchanged if the frequency is increased to 3.69×10^5 ." This indicates that the magnetons are in extremely rapid equilibrium with thermal energy.

The question as to why heat effects have not been observed by experimenters making magnetic measurements suggests itself. An amount of material containing only about 0.001 gram atom of gadolinium was used and this was in thermal contact with the bath by means of hydrogen or helium gas conduction. It would thus seem that the effect could hardly have been sufficient to be distinguished from those possible due to lack of ordinary thermal distribution in the powdered material.

⁸ Onnes and Oosterhuis, *Comm. Phys. Lab. Leiden*, No. 139c

⁹ Breit and Onnes, *ibid.*, No. 168c

Some Applications

Bohr Magnetron Number.—The very successful low temperature investigation of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was started by Kamerlingh Onnes with the idea of obtaining the approach to saturation and thus a direct determination of the magnetic moment. This was possible only because of the high magnetic moment of the gadolinium atom. It would now seem possible to extend this method to other less magnetic substances with the assistance of cooling by relatively larger amounts of a substance with high magnetic moment. As was first pointed out by Onnes in connection with cryogenic work of this kind, the intensity of magnetization being a function of M/T , our inability to obtain very large fields combined with the fact that values of the magnetic moment are small may be overcome by lowering the temperature.

Electrical and Thermal Conductivity.—The investigation of thermal and supraconductivity at still lower temperatures may throw light on certain underlying principles and mechanisms which are as yet somewhat obscure, to say the least. The heat flow for measuring thermal conductivity could conveniently be supplied by the field and a magnetic substance if properly controlled. Further study of the lowering of the temperature at which supraconductivity begins when a magnetic field is applied should prove profitable.

Calorimetry.—Woltjer and Onnes^{7c} have suggested the use of magnetic susceptibility for thermometric purposes. The following method of determining heat capacities at suitable temperatures would seem capable of development to a considerable degree of accuracy. (1) Isothermal magnetization of a working substance in thermal contact with a bath and the material to be investigated. (2) Adiabatic demagnetization of the working substance plus the material investigated to various final field strengths. (3) Measurement of the forces due to a small fraction of the paramagnetic material located in the magnetic gradient as a means of determining both initial and final temperatures.

The possibilities of this method will be more evident when the quantum treatment given to the effects concerned is considered. This will be found in the following paper. By such a method the question of zero-point entropy for supercooled liquids such as glycerol¹⁰ could be still further investigated.

The orientation of di-poles in an electric field presents an analogous phenomenon to that which we have been discussing, but the orientation of a di-pole would probably involve the turning of a molecule in a solid. While this turning is one which might take place through some small angle, especially where the crystal consists of simple molecule units, it

¹⁰ Gibson and Giauque, *THIS JOURNAL*, **45**, 93 (1923). Simon and Lange, *Z. Physik*, **38**, 227 (1926).

seems unlikely that such an effect would be accompanied by a sufficiently large entropy change to be useful for such purposes as those considered. However, there are few data on this point.

Summary

A thermodynamic treatment of certain magnetic phenomena has been given.

The entropy change accompanying the magnetization of paramagnetic substances and its application to obtaining temperatures below 1°K. has been discussed.

Some remarks have been made concerning the analogous case of di-pole orientation in an electric field.

Some suggestions have been made concerning the application of temperatures obtainable to the direct determination of the number of magnetons in paramagnetic substances, the further investigation of thermal and superconductivity, and a method suitable for the determination of heat capacities below 1°K.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

PARAMAGNETISM AND THE THIRD LAW OF THERMODYNAMICS. INTERPRETATION OF THE LOW-TEMPERATURE MAGNETIC SUSCEPTIBILITY OF GADOLINIUM SULFATE

BY W. F. GIAUQUE

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It is the primary purpose of this article to show that the ordinary method of obtaining an absolute value of the entropy of a substance by means of the third law of thermodynamics is not always applicable to paramagnetic substances. It is also desired to show how the present method may be extended to correct for the paramagnetism in such cases.

Before proceeding to do this it will be desirable to interpret the measurements of Woltjer and Onnes¹ on the magnetic properties of gadolinium sulfate, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, in order that this substance may be used as an example for discussion.

Onnes and Woltjer show that their data follow the equation of Langevin² but express some surprise at the magnitude of the deviations. However, they did not feel able to claim that the difference was beyond the error of experiment. A decidedly systematic trend is noticeable in their observed minus calculated differences.

According to Langevin, the molal intensity of magnetization $I = M / (\coth M\mu / RT - RT / M\mu)$, where M is the molal magnetic moment, μ

¹ Woltjer and Onnes, *Comm. Phys. Lab. Leiden*, No. 167c.

² Langevin, *Compt. rend.*, 140, 1171 (1905).

the magnetic field strength, R the molal gas constant and T the absolute temperature. It may readily be shown by methods given in the preceding article that for a Langevin substance the entropy change during magnetization from zero field to field H is

$$\Delta S = R \left[\ln \frac{\sinh \frac{MH}{RT}}{\frac{MH}{RT}} - \frac{MH}{RT} \coth \frac{MH}{RT} \right]_{H=0}^{H=H}$$

which indicates that the entropy decreases to negative infinity as the field is increased without limit. This is obviously due to the fact that Langevin assumed the existence of a continuous series of orientations with respect to the applied field.

Pauli³ has shown that the initial susceptibility of paramagnetic substances is best explained by the application of Langevin's method and the assumption of a small number of possible orientations. This latter can hardly be considered an assumption in view of the multiplicity observed in the Zeeman effect and the splitting of a stream of paramagnetic atoms passed through a magnetic gradient first observed by Gerlach and Stern.⁴

At the time Pauli first tested his proposal the anomalous Zeeman effect had not been sufficiently interpreted to enable the choice of the correct number of possible orientations in the various cases. However, the solution of this problem appears to be in a fairly satisfactory state at present.

Pauli's treatment of magnetic susceptibility has been for the limiting case as the field approaches zero, since at room temperature the values are independent of field strength within the limit of experimental error. However, at low temperatures this is no longer the case, and it will be necessary to derive the complete expression.

Hund⁵ has shown that for the trivalent gadolinium ion the inner quantum number j is $7/2$, while the ratio of magnetic over mechanical moment g is 2 in this case. When j is $7/2$, eight spatial orientations with respect to the field are possible,⁶ four of which have clockwise and four counterclockwise rotation. All eight of these situations are taken as equally probable in the absence of an external field.

The four angles of orientation for a gadolinium ion are given by $\cos \Theta = j/j, (j-1)/j, (j-2)/j, (j-3)/j$, respectively, where Θ is the angle between the plane of rotation and a plane normal to the field.

The magnetic moment is gjM , where M is now taken as the moment of a molal unit Bohr magneton.

The torque exerted by the field = $gjM \sin \Theta$.

³ Pauli, *Physik. Z.*, 21, 615 (1920).

⁴ Gerlach and Stern, *Z. Physik*, 9, 349 (1922).

⁵ Hund, *ibid.*, 33, 855 (1925).

⁶ Sommerfeld, "Atombau und Spektrallinien," Vieweg, Braunschweig, 1922, 4th ed., p. 616.

The work done by the field when the magnetic moment is turned from Position Θ to the completely lined up position in Field \mathfrak{H} is $gjM\mathfrak{H}(1 - \cos \Theta)$ for those with the field, $gjM\mathfrak{H}(1 + \cos \Theta)$ for those against the field.

Then $N = Z \Sigma e^{-\frac{gjM\mathfrak{H}(1 - \cos \Theta)}{RT}} + e^{-\frac{gjM\mathfrak{H}(1 + \cos \Theta)}{RT}}$ where N is Avogadro's number and Z is the number of atoms entirely lined up; and

$$I = (Z/N) \Sigma gjM \cos \Theta \left[e^{-\frac{gjM\mathfrak{H}(1 - \cos \Theta)}{RT}} - e^{-\frac{gjM\mathfrak{H}(1 + \cos \Theta)}{RT}} \right]$$

$$= gjM \frac{\Sigma \cos \Theta \sinh \frac{gjM\mathfrak{H} \cos \Theta}{RT}}{\Sigma \cosh \frac{gjM\mathfrak{H} \cos \Theta}{RT}} \quad (1)$$

both summations being over all possible orientations. The above formula is general for all cases where $2j$ is odd, and the orientation is without restraint when $\mathfrak{H} = 0$. When $2j$ is even, a similar treatment leads to

$$I = gjM \frac{\Sigma \cos \Theta \sinh \frac{gjM\mathfrak{H} \cos \Theta}{RT}}{\frac{1}{2} + \Sigma \cosh \frac{gjM\mathfrak{H} \cos \Theta}{RT}} \quad (2)$$

The value of the magnetic moment is given by the equation $M = (e/m)(h/4\pi)N$ where e/m is the ratio of electronic charge to mass in electromagnetic units, and h is Planck's constant. Birge,⁷ after careful consideration of the available data, has adopted as the most probable values of the constants involved $e/m = 1.760 \times 10^7$ e. m. u.; $h = 6.560 \times 10^{-27}$ erg sec.; $N = 6.059 \times 10^{23}$. Thus, $M = 5567$, and for the gadolinium ion the total magnetic moment $gjM = 2 \times (7/2) \times 5567 = 38,970$, which is saturation value of this substance.

It has been shown by numerous experiments that the initial susceptibility of the gadolinium ion is within the limits of experimental error equal to that of $\frac{1}{2}\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ when corrections have been applied for the associated diamagnetic effect. The available data on this point have been summarized by Zernike and James.⁸ It might be expected that the definite arrangement of the atoms in a crystal lattice would influence the magnetic properties, but this is apparently not the case with $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

TABLE I

THEORETICAL FRACTIONAL MAGNETIC SATURATION OF $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

$\frac{gjM\mathfrak{H}}{RT}$	$I/I(\text{sat})$	$\frac{gjM\mathfrak{H}}{RT}$	$I/I(\text{sat})$
0.7	0.2877	4.2	0.8773
1.4	.5162	6.3	.9434
2.1	.6714	7.0	.9553
2.8	.7706		

⁷ Birge, *Science*, **64**, 180 (1926).⁸ Zernike and James, *THIS JOURNAL*, **48**, 2827 (1926).

Using Equation 1, values of $I/I_{(sat.)}$ for various values of gJM_{theor}/RT have been calculated. The results are given in Table I.

The experimental results of Woltjer and Onnes¹ on their Sample Gd II have been used to calculate values of $I_{\text{obs.}}/I_{38,970}$ and the results are given in Table II. The number of the experiment is also given to facilitate reference with the original work. Their results on Gd I have not been considered, since it is stated that they are less reliable.

TABLE II
EXPERIMENTAL $I/I_{38,970}$ FOR $\frac{1}{2}\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

Expt. no.	$T^\circ\text{K.}$	$\frac{38,970}{RT}$	$\frac{I_{\text{obs.}}}{I_{38,970}}$	Expt. no.	$T^\circ\text{K.}$	$\frac{38,970}{RT}$	$\frac{I_{\text{obs.}}}{I_{38,970}}$
4	4.20	0.2906	0.1228	12	2.30	2.701	0.7719
5	4.20	.2906	.1238	13	1.48	4.159	.8597
6	4.20	.5668	.2450	15	1.48	4.159	.8603
3	4.20	.8466	.3518	14	1.48	5.365	.9021
7	4.20	1.116	.4408	34	1.41	0.4720	.2066
2	4.20	1.510	.5516	33	1.41	0.6239	.2677
8	4.20	1.510	.5525	32	1.41	0.7707	.3348
28	4.20	1.511	.5505	31	1.41	4.343	.8778
9	4.20	1.791	.6088	30	1.41	5.185	.9046
1	4.20	1.930	.6413	29	1.41	5.804	.9320
10	4.20	1.930	.6400	36	1.31	6.047	.9343
11	3.40	1.852	.6341	35	1.31	6.266	.9403

The experimental data are compared with the theoretical curve in Fig. 1. The agreement is very satisfactory, particularly when it is considered that

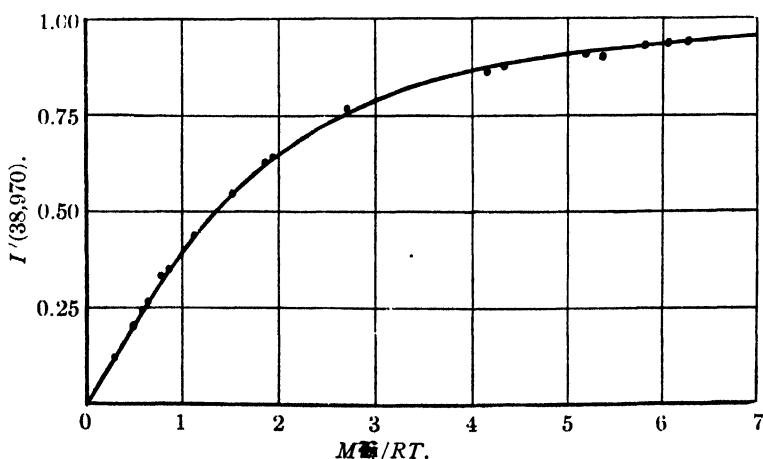


Fig. 1.

the theoretical curve is calculated from natural constants whose values are in no way dependent on the work of Onnes and Woltjer.

The calculation of the theoretical value of the entropy of magnetization

may be carried out by a method used by Tolman and Badger⁹ to obtain the rotational entropy of diatomic gases.

Let $gjM\hbar/RT = a$ and $Q = \sum \cosh(a \cos \Theta)$. Then $dQ/da = \sum \cos \Theta \sinh(a \cos \Theta)$, and $I = gjM d \ln Q/da$. From the preceding paper, $(\partial S/\partial \hbar)_T = (\partial I/\partial T)_\hbar$. Therefore,

$$\begin{aligned} \left(\frac{\partial S}{\partial \hbar}\right)_T &= -\frac{a^2 R}{\hbar} \left(\frac{\partial^2 \ln Q}{\partial a^2}\right)_\hbar \\ \Delta S &= -R \int_0^\hbar \frac{a^2}{\hbar} \frac{\partial^2 \ln Q}{\partial a^2} d\hbar = R \left[\ln Q - a \frac{d \ln Q}{da} \right]_0^\hbar \\ &= R \left[\ln \sum \cosh \frac{gjM\hbar \cos \Theta}{RT} - \ln 4 - \frac{gjM\hbar}{RT} \frac{\sum \cos \Theta \sinh \frac{gjM\hbar \cos \Theta}{RT}}{\sum \cosh \frac{gjM\hbar \cos \Theta}{RT}} + 0 \right] \quad (3) \end{aligned}$$

The ΔS for various values of a has been calculated by means of Formula 3 and the results are tabulated in Table III. The limiting case for large values leads to $-R \ln 8$ as of course it must, since eight positions were assumed equally probable in zero field, while only one is possible for the case $a = \infty$. Thus, when 0.5 mole of $Gd_2(SO_4)_3 \cdot 8H_2O$ initially in zero field is completely saturated the entropy change is -4.14 cal. per degree. It may be noted that when $a = 7$, $\hbar = 19,420$ when $T = 1.3^\circ K$.

TABLE III

THEORETICAL ENTROPY OF MAGNETIZATION OF $\frac{1}{2}Gd_2(SO_4)_3 \cdot 8H_2O$			
a	$-\Delta S$, cal./deg.	a	$-\Delta S$, cal./deg.
0.7	0.196	4.2	2.398
1.4	.664	6.3	3.066
2.1	1.196	7.0	3.223
2.8	1.674	∞	4.135

The use of a nearly perfect paramagnetic substance and Langevin's equation for thermometric purposes as suggested by Woltjer and Onnes¹ might be more accurately carried out if Equations 1 or 2 were substituted, depending on the character of the substance used.

Equation 3 might be used for calculation of the heat effect in the magnetic method of mixtures, proposed in the preceding article, for the measurement of heat capacities below $1^\circ K$.

A substance obeying Equation 1 would be a strong magnet if cooled to the absolute zero in any finite field. It is interesting to note that could the substance be taken to the absolute zero in the absence of any field the entropy change, if subsequent magnetization took place, would be finite. This is in some respects similar to the entropy change accompanying unmixing of the constituents of solutions, in this case the mixing (demagnetization) and unmixing (magnetization) being under the control of a field. However, if the atoms affected each other in a ferromagnetic sense the substance would become a saturated magnet even in the absence of a field.

⁹ Tolman and Badger, THIS JOURNAL, 45, 2277 (1923).

The low-temperature deviations of paramagnetic substances from Curie's law are seldom of a ferromagnetic nature. The formula $\chi(T + \Delta) = C^{10}$ represents a large share of the initial susceptibility data surprisingly well, the values of Δ being positive in most cases. This leads at low temperatures to a susceptibility which is nearly independent of temperature, making it seem probable that such substances would approach the absolute zero without appreciable magnetization.

We may take the case of solid oxygen as an example of a substance which, while remaining strongly paramagnetic, would not become a magnet as the absolute zero is approached, since it has been shown by Perrier and Onnes¹¹ that the initial susceptibility of the form stable at the temperatures of liquid hydrogen is practically without temperature coefficient.

As the third law of thermodynamics has been used, entropy is calculated by the integration of specific heat with respect to the natural logarithm of temperature plus what has seemed a plausible extrapolation beyond the lowest temperature measured. When the above method is used the entropy due to the distribution of magnetic moment in the various possible states will sometimes be included, but will more often be neglected.

In view of our limited knowledge concerning atomic structure the assignation of an absolute value to the entropy of a substance would seem to be a somewhat uncertain procedure. However, for the purposes of chemistry it will be sufficient if all effects which may be produced by chemical reactions are considered.

Lewis¹² has called attention to the importance of magneto-chemical effects and one may refer to his publications for a discussion of this subject. While reactions involving a change in magnetic moment are considerably in the minority they are by no means infrequent, for example, the reactions of oxygen. Lewis has suggested that strained conditions which may be an essential part of certain types of chemical bonds may lead to only partial balancing of magnetic moment. Many chemical as well as magnetic observations support this view. In such cases the definite positions of the constituent magnetons would lead to no randomness or entropy of the type here considered. This type of paramagnetism should be practically without temperature coefficient.

Ewing¹³ reconsidering his theory of ferromagnetism has discussed a very plausible explanation requiring in part random and in part fixed distribution of the magnetons in ferromagnetic substances. We presume that the fixed magnetons would be of the valence type although all electrons of the valence group may not be fixed.

¹⁰ Onnes and Oosterhuis, *Comm. Phys. Lab. Leiden*, No. 129b.

¹¹ Perrier and Onnes, *ibid.*, No. 139c.

¹² Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, 1923; *Chem. Rev.*, 1, 231 (1925).

¹³ Ewing, *Phil. Mag.*, 43, 493 (1922).

Langmuir¹⁴ mentions the possibility of interchange of electrons between the valence and kernel groups in the case of transition elements such as iron, cobalt and nickel. This seems to be consistent with both chemical and magnetic facts. This adds to the complication in these cases, especially if thermodynamic equilibrium exists between the various possibilities. This seems quite likely in some cases.

Parks and Kelley,¹⁵ in measuring the heat capacity of magnetite, Fe_3O_4 , have found a marked heat absorption in the region about 113–117°K., which they attribute to some magnetic change. It would thus be unsafe to correct for the magneton entropy on the basis of data obtained at ordinary temperatures without investigating the nature of this change. Millar, in an unpublished investigation on the same substance, has found that the heat absorption extends over a range of at least 20°.

The systems which we have been discussing are typical of those which the spectroscopist classes as degenerate, but which can be made undegenerate by the application of a magnetic, electric or gravitational field, as the case may be. It will be recalled that the adiabatic hypothesis of Ehrenfest¹⁶ or, as it has been called by Bohr, the principle of mechanical transformability, does not necessarily hold for degenerate systems. The existence of the earth's magnetic, electric and gravitational fields will presumably keep the various degrees of freedom concerned undegenerate for ideal systems. Assuming the ideal case to hold for actual systems, thus making $S = \int_0^1 C \, d \ln T$, where C represents the heat capacity, the practical difficulty still remains that the thermal effects associated with magnetic saturation by the earth's field, for example, would occur principally below 1×10^{-5} °K. This makes a knowledge of the magnetic properties necessary in order to consider the contribution to the entropy due to unbalanced magnetic moment.

Lewis and Gibson¹⁷ have stated that the entropy of perfect crystalline substances approaches zero at the absolute zero of temperature. A crystalline substance with random distribution of magnetic moment could not be considered perfect even though the effect on the atomic centers is practically negligible. Thus, our conclusions are in accord with those of the above authors.

We have discussed the data of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ in order to add to the reality of our statements, but in the reactions of gadolinium during which it remains trivalent it is obvious that the entropy due to magnetic moment would cancel.

¹⁴ Langmuir, *THIS JOURNAL*, **41**, 879 (1919).

¹⁵ Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

¹⁶ Ref. 6.

¹⁷ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

In the general case the amount of entropy $R \ln (1 + 2j)$ should be added to the entropy due to other causes; j is the number of units of resultant angular mechanical momentum of the unit which can be oriented. It is the mechanical rather than the magnetic moment which determines the number of possible positions. At the present time we believe there are no equilibrium, heat-capacity and magnetic data of sufficient completeness and accuracy to serve as a test of the above statement. The amount is 1.38 cal. per degree for one-half and 2.18 cal. per degree for one unit of resultant angular momentum.

Summary

The low-temperature magnetic susceptibility data of gadolinium sulfate, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, have been shown to agree quantitatively with an equation, using natural constants and based on orientation without restraint within the solid.

The theoretical entropy changes accompanying the application of a magnetic field are considered.

It is suggested that the magnetic formulas proposed be used in connection with Woltjer and Onnes' suggestion of paramagnetic thermometry. It is also suggested that they be used in connection with the magnetic mixture method of low temperature calorimetry as previously suggested by this author.

Assuming that the entropy of a perfect crystalline substance is zero at the absolute zero of temperature, it is shown that it is not always feasible to obtain an absolute value of entropy from heat-capacity data alone in the case of substances with a positive susceptibility.

It is shown how to correct for the above deficiency when the number of units of unbalanced mechanical moment is known from magnetic data on the form of the substance existing at temperatures low enough to permit sufficiently accurate extrapolation of the heat-capacity curve resulting from ordinary thermal effects.

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No. 551]

SODIUM MONOMETAPHOSPHATE AND ITS ACID HYDRATION

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The hydration of metaphosphoric acid to orthophosphoric acid or a metaphosphate to the orthophosphate, as $\text{NaPO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaH}_2\text{PO}_4$, has attracted the attention of chemists ever since the epochal work of Graham.¹ Much work has been done but the problem is not completely solved. Graham was aware of some of the difficulties to be encountered. In his work he states, "The problem is, therefore, environed with difficulties." These difficulties are twofold. First, metaphosphoric acids or their salts are not well understood. It is thought that polymers exist, the preparation of which has not been thoroughly investigated, and the decision as to their forms has been based mainly upon their methods of preparation or empirical formulas rather than upon experimental evidence. Second, the rate of hydration must be ascertained by the measurement, at intervals, of either the concentration of the metaphosphate left unchanged in the solution or the concentration of the orthophosphate formed during the progress of the reaction. On account of the widely differing solubilities of the so-called polymeric forms of the metaphosphates, the direct determination involving an actual separation of the ortho- from the metaphosphoric acid is by no means easy. This separation is actually necessary in order to study the factors influencing the hydration.

In order to understand this reaction better the two above-mentioned difficulties must be overcome as far as possible. This requires, as a basic consideration, that a salt of well-established identity be prepared and its hydration studied. Furthermore, the definite salt must be readily and quantitatively separable from the substances formed during the hydration.

Heretofore the methods employed in the study of the hydration of metaphosphoric acid have been to a great extent indirect, and the acid used was prepared by dissolving phosphorus pentoxide in cold water, by dehydrating orthophosphoric acid or by preparing a heavy metal salt from which a solution of the metaphosphoric acid was obtained by precipitating the metal with hydrogen sulfide. Acidimetry was used by Sabatier,² Montemartini and Egidi,³ Berthelot and André⁴ and Balareff;⁵ thermochemistry by Giran,⁶ gravimetric analysis by Holt and Meyers;⁷

¹ Graham, *Phil. Trans.*, **123**, 253 (1833).

² (a) Sabatier, *Compt. rend.*, **106**, 63 (1888); (b) **108**, 734, 804 (1889).

³ Montemartini and Egidi, *Gazz. chim. ital.*, **31**, I, 394 (1901).

⁴ Berthelot and André, *Compt. rend.*, **124**, 261 (1897).

⁵ Balareff, *Z. anorg. Chem.*, **72**, 85 (1911).

⁶ Giran, *Compt. rend.*, **135**, 1333 (1902).

⁷ Holt and Meyers, *J. Chem. Soc.*, **99**, 384 (1911).

change of index of refraction by Blake and Blake;⁸ change of conductivity by Prideaux;⁹ and change of the lowering of the freezing point by Holt and Meyers.¹⁰

In their gravimetric method Holt and Meyers precipitated the unchanged meta- in the presence of ortho- and pyrophosphates as a barium metaphosphate bearing the empirical formula $\text{Ba}(\text{PO}_3)_2$. By repeated experiments with mixtures of ortho-, pyro- and metaphosphates, they claim very little variation in the composition of their precipitate. Judging from the irregularity of the curve they publish it seems that their method is open to question or fraught with a considerable error.

Other attempts to apply methods of precipitation were employed to show whether or not pyrophosphoric acid was formed during the process of hydration.¹¹ These methods are not applicable to the problem, for on the one hand, the method of Berthelot and André requires the heating of the solution to be analyzed, acidified with acetic acid, on a boiling water bath for three or four hours to secure the formation of an uncertain magnesium ammonium pyrophosphate, a treatment entirely out of the question in view of the marked effects of temperature and hydrogen ion upon the rate of hydration; on the other hand, the precipitation of pyrophosphate of copper or cadmium in an acetic acid solution, the method employed by Balareff, is not free from doubt because upon it he based his contention that no pyrophosphate as an intermediate product was formed during the hydration, a statement not in harmony with his later work.¹²

Moreover, there have been two different opinions as to whether pyrophosphoric acid was formed as an intermediate product during the hydration of meta- to orthophosphoric acid. One group of chemists maintained that the hydration was direct to ortho-, while another claimed pyrophosphoric acid as an intermediate product. The former was supported by Graham,¹ Sabatier,¹³ Montemartini and Igidi³ and Balareff,¹⁴ while Berthelot and André,¹⁵ Giran,¹⁶ Holt and Meyers,¹⁰ and Balareff¹² adhered to the latter.

Accordingly, a method has been devised and materials prepared for the attack of this problem whereby the conditions and factors influencing the reaction may be studied to a better advantage by direct, standard analytical methods. An account of the investigation follows.

⁸ Blake and Blake, *Am. Chem. J.*, 27, 68 (1902).

⁹ Prideaux, *Chem. News*, 99, 161 (1909).

¹⁰ Ref. 7, p. 385; *ibid.*, 103, 532 (1913).

¹¹ Balareff, *Z. anorg. Chem.*, 68, 266 (1910); Ref. 4.

¹² Balareff, *Z. anorg. Chem.*, 96, 103 (1916).

¹³ Ref. 2 (a).

¹⁴ Balareff, *Z. anorg. Chem.*, 67, 234 (1909). Ref. 11, p. 288.

¹⁵ Berthelot and André, *Compt. rend.*, 123, 776 (1896); 124, 265 (1897).

¹⁶ Giran, *J. Russ. Phys.-Chem. Soc.*, 135, 1333 (1902).

Apparatus

The apparatus used to measure the concentration of hydrogen ion has been described by Hansen and one of us.¹⁷

Preparation of Materials

Monosodium Phosphate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$.—A quantity of the purest monosodium phosphate obtainable was crystallized thrice from distilled water. The precipitation was accomplished each time by adding to the aqueous solution an equal volume of redistilled 95% alcohol and cooling in ice water. The final product was obtained quite free from moisture by washing by suction on a Büchner funnel thrice each with absolute alcohol and absolute ether. To remove the ether it was exposed to the air for a short time on a clean surface. The dihydrate was thus obtained. Its high dissociation pressure prevented other methods of drying and required hermetically sealed bottles as containers.

The following analyses were made for water of hydration:

Lot	Sample	Water of hydration plus water of constitution, %
1	1	34.47
1	2	34.52
2	1	34.73

The theoretical percentage for the hydrate $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is 34.63.

Sodium Monometaphosphate, NaPO_3 .—Sodium monometaphosphate was prepared by dehydrating the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ as above prepared in a calibrated electric furnace. The hydrate in a large platinum crucible was held at a temperature of 200° for an hour. The temperature was then slowly raised during the next hour till the mass melted to a clear liquid. It was held at this temperature—approximately 600° —for ten minutes. Finally, the temperature was lowered to 450° and maintained at this point for two hours while the substance crystallized. At the end of this crystallization the metaphosphate was quickly cooled by dipping the bottom of the crucible in cold water.

The sodium metaphosphate above prepared was investigated by the freezing-point method with the following results.

Sodium metaphosphate, g.	Water, g.	F. p. depression	Mol. wt.
5.0472	100	0.916	102.5
2.8159	100	.546	95.9
1.3435	100	.351	86.9

These depressions indicate a sodium metaphosphate whose molecular weight corresponds to the formula NaPO_3 (Theoretical—102.04). The above sodium monometaphosphate was formerly prepared in a somewhat similar way¹⁸ from sodium ammonium hydrogen phosphate by heating the resulting vitreous mass from fusion till it crystallized or by slow cooling from fusion. By taking 2.77 g. of their crystals in 100 cc. of water, Holt and Meyers obtained a depression of $.51^\circ$, which corresponds to a molecular weight of 102 and a formula of NaPO_3 .

An optical study of the sodium monometaphosphate made by Professor R. J. Colony of the Department of Geology of Columbia University confirms our belief that the sodium monometaphosphate prepared above is

¹⁷ Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926).

¹⁸ Tanatar, *J. Russ. Phys.-Chem. Soc.*, **30**, 99 (1898); Ref. 10 (b), p. 535.

a distinct chemical individual. Through the kindness of Professor Colony we are permitted to publish the following optical properties: "It has an index of refraction: $N_g = 1.486 \pm 0.005$, $N_p = 1.473 \pm 0.005$, birefringence $N_g - N_p = 0.013 \pm 0.005$. It is apparently monoclinic, optically negative and biaxial with a large optical angle. It shows uniformity in behavior, form and composition."

Sodium monometaphosphate is soluble in water. It reacts acid to litmus—a property described by Graham,¹ the explanation for which is not apparent. From a 0.3 *M* solution white, flocculent precipitates, which change to crystalline form on standing, may be obtained from solutions of the nitrates of silver, lead, mercury and bismuth. With solutions of the nitrates of zinc, cadmium, cobalt, nickel and copper, white amorphous precipitates are formed. It does not give a precipitate in a solution containing magnesium chloride, ammonium chloride and ammonium hydroxide in moderately high concentrations. This property was employed in the separation of monometaphosphoric acid from orthophosphoric acid.

Other Chemicals.—The hydrochloric acid, potassium chloride and mercurous chloride used were prepared according to the description given by Hansen and one of us.¹⁷

Method of Procedure

In planning a method of procedure the factors influencing the reaction have as far as possible been either measured or controlled. The temperature, the concentration of sodium monometaphosphate, the concentration of orthophosphate, the possible formation of pyrophosphate and the concentration of hydrogen ion are the variable factors which influence the hydration of sodium monometaphosphate.

The temperature was regulated and controlled at $45^\circ \pm 0.01^\circ$. The ortho- was separated from the metaphosphoric acid and determined directly. By difference the unchanged meta- was obtained. No satisfactory quantitative method has as yet been found whereby pyrophosphoric acid may be determined in mixtures such as occur in this investigation. Therefore, an estimate by other means of the amount formed is all that is possible. The concentration of hydrogen ion was measured at intervals during the hydration.

Preparation of Solutions.—All solutions were prepared at 20° . The requisite amount of sodium monometaphosphate was dissolved in water in a volumetric flask. To this was added with constant rotation to avoid local excess the amount of hydrochloric acid necessary to furnish the desired hydrogen-ion concentration. The solution was then diluted to volume as quickly as possible. After thorough mixing, the solution was put in a "non-sol" bottle and placed in the bath. The whole operation, beginning with the addition of the acid, required not more than ten minutes.

The specific gravity of each solution was taken at 20° by means of a Westphal

balance at the beginning of the reaction and again at the end. No change of volume was observed during the hydration greater than one part in one thousand. Hence one specific gravity measurement for each solution sufficed for calculating the amount of metaphosphate transformed to orthophosphate. The concentrations of the solutions were all expressed in moles per liter. Therefore, knowing the specific gravity and the concentration, the amount of sodium monometaphosphate in any weighed quantity of solution could be determined.

The Separation of Monometaphosphoric Acid from Orthophosphoric Acid.—Orthophosphoric acid was separated from monometaphosphoric acid by means of "magnesia mixture" in a cold solution. As previously stated, a solution of sodium monometaphosphate does not give a precipitate with "magnesia mixture" in concentrations used in this procedure—and in fact very much higher concentrations. This method of separation has been tested both qualitatively and quantitatively. Seventenths of a gram of sodium monometaphosphate together with 25 cc. of standard "magnesia mixture" in a total volume of 125 cc. was allowed to stand for 24 hours repeatedly and no precipitate appeared, while a precipitate of the orthophosphate appeared immediately in another solution similarly treated, excepting that 1 mg. of phosphorus in the form of orthophosphate was added. It remains now to be shown that monometaphosphoric acid is quantitatively separable from the orthophosphoric acid and that no appreciable hydration occurs during the time of standing required for the precipitation of the magnesium ammonium phosphate. Thirty determinations of orthophosphate according to the method outlined below, in the presence of varying quantities of sodium monometaphosphate from 900 mg. to 100 mg., have been made. The amount of orthophosphate used has varied and the times of standing have been 6, 12 and 18 hours, respectively. There was an increase in amount found over the amount added which was of the same order irrespective of the time of standing. This shows that hydration was not the cause of the increase; for if it had been, the amount of increase would have been a direct function of the time. This increase not due to hydration was inherent in the method and doubtless caused by adsorption and subsequent hydration by the acid used to dissolve the precipitate. The magnitude of the error from this source was found by the above determinations to be on the average not greater than ten parts per thousand for amounts of sodium monometaphosphate not exceeding 300 mg.

Determination of Orthophosphate.—Orthophosphate was determined by the standard gravimetric method. The samples of the solution were taken by means of Bailey weighing burets. Before precipitation each sample was diluted to 100 cc. Twenty-five cc. of "magnesia mixture" was then added, which made the final volume 125 cc. The separation of the magnesium ammonium phosphate precipitate from the unprecipitated meta- was made by filtration not more than 16 hours nor less than 6 hours after the first precipitation. After separating and washing with an ammonium hydroxide-ammonium nitrate solution, the orthophosphate precipitate was dissolved with hot hydrochloric acid and reprecipitated. Finally, after 12 hours' standing, the magnesium ammonium phosphate was filtered through a weighed Gooch crucible and weighed as magnesium pyrophosphate. By this method the amount of the monometaphosphate transformed to ortho- could be determined.

In the hydrations where the concentration of acid was high, the analytical results varied somewhat at the beginning of each hydration. The variation was due to the simultaneous precipitation of a gelatinous substance which contaminated the magnesium ammonium phosphate. This gelatinous precipitate was soluble in an excess of magnesium salts and from its behavior indicated that it was magnesium pyrophosphate. The pyrophosphate was formed during the hydration. The concentration

of hydrogen ion showing abnormally low values for the high acid concentrations indicated further that pyrophosphate was probably formed. With no satisfactory quantitative method for separating pyro- from orthophosphate and determining it, the difficulty was met by preventing its precipitation by the addition of an excess of "magnesia mixture" a method which was on the whole quite successful.

Measurement of Concentration of Hydrogen Ion.—All hydrogen-ion concentration measurements were made at 45° by the apparatus and method described by Hansen and one of us.¹⁷ The calculations were made by use of the formula $\log C_{H^+} = (0.2342 - E)/0.063$.

Experimental Data

The following table gives the concentrations and the densities of the solutions selected for investigation.

TABLE I

	D	E	H	K	O	Z	S
Molar concn., NaPO ₃	0.500	0.500	0.500	0.300	0.100	0.300	0.300
Molar concn., HCl.....	.483	.339	.192	.339	.339	.010	.000
d ₂₀ /d ₂₀	1.044	1.042	1.041	1.025	1.011	1.025	1.025

All hydrations except the Z and S were made in duplicate. Duplicate samples of the two exceptions were taken. The mean deviation of the results in duplicate is not greater than five per cent. when the concentration of pyrophosphate is high at the beginning nor greater than one per cent. when the hydration nears completion.

TABLE II

SOLUTIONS D, C*, E AND H
0.500 M NaPO₃

	Sample	Time, hours	Percentage hydrated	Voltage	(H ⁺)
Soln. D 0.483 M HCl	1	1.75	8.3	0.2716	2.55 × 10
	2	4.67	47.1	.2785	1.98
	3	10.67	66.0	.2834	1.66
	4	24.17	81.6	.2881	1.39
	5	48.42	87.9	.2923	1.20
	6	72.92	92.7	.2946	1.10
	7	120.17	96.7	.2970	1.01
	8	168.70	98.4	.2979	0.95
Soln. C* 0.483 M HCl	1	3.17	45.9	0.2754	2.22 × 10
	2	6.17	50.0	.2797	1.82
	3	10.17	67.8	.2830	1.68
	4	16.17	67.8	.2842	1.61
	5	25.17	81.6	.2888	1.42
	6	37.17	82.8	.2909	1.26
	7	49.17	88.2	.2922	1.20
	8	72.17	91.0	.2937	1.13
	9	121.17	98.0	.2963	1.03
	10	169.17	99.7	.2978	0.98

* The values for solution C, which is a duplicate of solution D, are given to show the reproducibility of measurements.

TABLE II (Concluded)

	Sample	Time, hours	Percentage hydrated	Voltage	(H ⁺)
Soln. E 0.339 M HCl	1	2.17	7.6	0.2856	15.28 × 10 ⁻²
	2	5.17	25.8	.2930	11.66
	3	11.17	50.3	.3005	8.86
	4	23.17	67.4	.3073	6.91
	5	48.58	75.1	.3144	5.30
	6	71.42	80.5	.3176	4.74
	7	119.05	84.3	.3214	4.13
	8	167.00	91.1	.3242	3.73
	9	239.42	95.7	.3262	3.47
	10	383.42	102.8	.3276	3.29
Soln. H 0.192 M HCl	1	6.20	13.8	0.3150	5.22 × 10 ⁻²
	2	13.37	24.5	.3224	3.98
	3	23.48	44.9	.3300	3.02
	4	47.30	63.4	.3383	2.28
	5	71.20	69.2	.3432	1.91
	6	119.31	73.4	.3486	1.53
	7	167.60	80.6	.3520	1.35
	8	192.53	78.1	.3533	1.29
	9	215.30	82.4	.3545	1.23
	10	263.70	85.1	.3562	1.16
	11	335.70	85.8	.3579	1.09
	12	457.10	92.3	.3596	1.02
	13	678.60	96.0	.3613	0.96
	14	875.30	98.4	.3625	.92

TABLE III

SOLUTION O

0.100 M NaPO₃, 0.339 M HCl

Sample	Time, hours	Percentage hydrated	Voltage	(H ⁺)
1	1.50	11.8	0.2715	2.56 × 10 ⁻¹
2	3.00	42.1	.2719	2.52
3	7.17	69.1	.2728	2.44
4	13.17	79.1	.2740	2.34
5	24.17	88.3	.2750	2.25
6	47.67	96.2	.2760	2.17
7	72.17	97.9	.2764	2.14

TABLE IV

SOLUTION K

0.300 M NaPO₃, 0.339 M HCl

Sample	Time, hours	Percentage hydrated	Voltage	(H ⁺)
1	1.50	9.2	0.2789	19.52 × 10 ⁻²
2	3.00	36.1	.2805	18.41
3	7.00	58.8	.2842	16.08
4	15.00	65.2	.2889	13.54
5	27.00	73.5	.2932	11.63
6	51.00	86.2	.2973	9.96

TABLE IV (Concluded)

Sample	Time, hours	Percentage hydrated	Voltage	(H ⁺)
7	83.42	93.9	.2990	9.36
8	120.17	96.3	.2996	9.14
9	168.42	97.4	.3000	9.03
10	240.02	98.6	.3002	8.96

TABLE V

SOLUTION Z

0.300 M NaPO₃, 0.010 M HCl

Sample	Time, days	Percentage hydrated	Voltage	(H ⁺)
1	0.03	..	0.3637	87.99×10^{-7}
2	.32	..	.3777	52.75
3	.82	..	.3829	43.64
4	1.83	..	.3896	34.15
5	3.01	..	.3960	27.02
6	5.01	..	.4039	20.25
7	6.93	12.2	.4088	20.26
8	13.88	25.3	.4200	11.24
9	20.88	42.0	.4271	8.67
10	27.71	48.7	.4325	7.12
11	39.67	58.2	.4393	5.55
12	57.75	72.9	.4451	4.49
13	93.67	87.3	.4488	3.92
14	122.70	93.3	.4507	3.66
15	144.56	97.1	.4521	3.48

TABLE VI

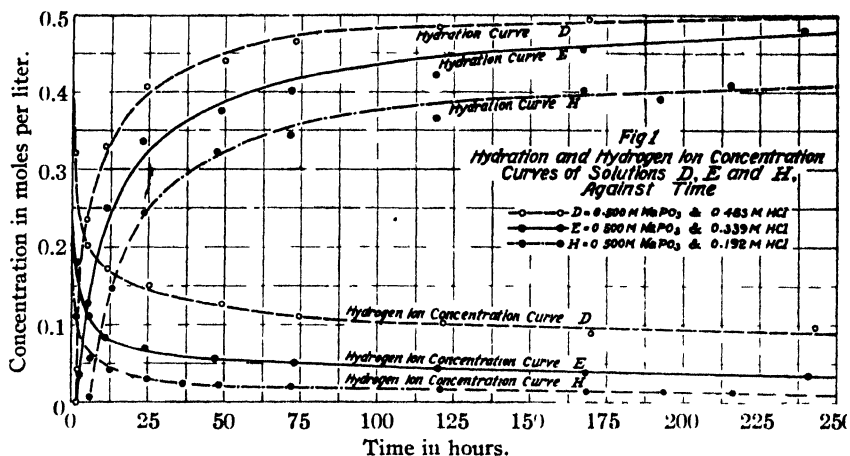
SOLUTION S

0.300 M NaPO₃, 0.000 M HCl

Sample	Time, days	Percentage hydrated	Voltage	(H ⁺)
1	0	..	0.6267	0.59×10^{-6}
2	1.00	..	.6037	1.37
3	2.00	..	.5894	2.30
4	4.00	..	.5776	3.54
5	5.00	..	.5739	4.05
6	7.00	..	.5678	5.07
7	10.00	..	.5608	6.54
8	15.00	..	.5522	8.96
9	20.00	..	.5460	11.41
10	25.00	1.8	.5412	13.39
11	45.00	5.2	.5292	20.55
12	60.00	7.5	.5258	23.52
13	74.00	10.4	.5231	25.96
14	88.00	13.2	.5212	27.82
15	109.00	19.6	.5191	30.06
16	149.00	32.3	.5157	34.02
17	177.00	41.4	.5132	37.28
18	200.00	49.1	.5109	40.64

Discussion

The Change of Concentration of Hydrogen Ion.—The data in the foregoing tables and the curves in the accompanying figures given as example show that there was a considerable decrease in the concentration of hy



drogen ion in all cases when hydrochloric acid was added to the solution in the beginning. This decrease was progressive and became less pronounced as the transformation of the meta- to orthophosphate becan

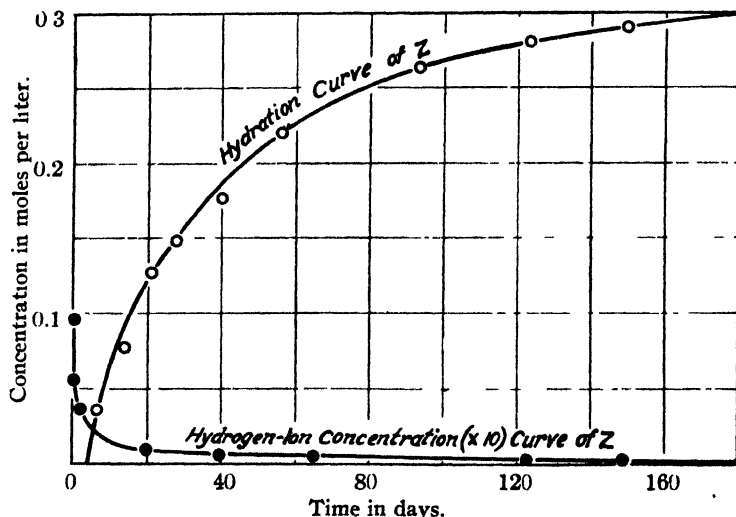


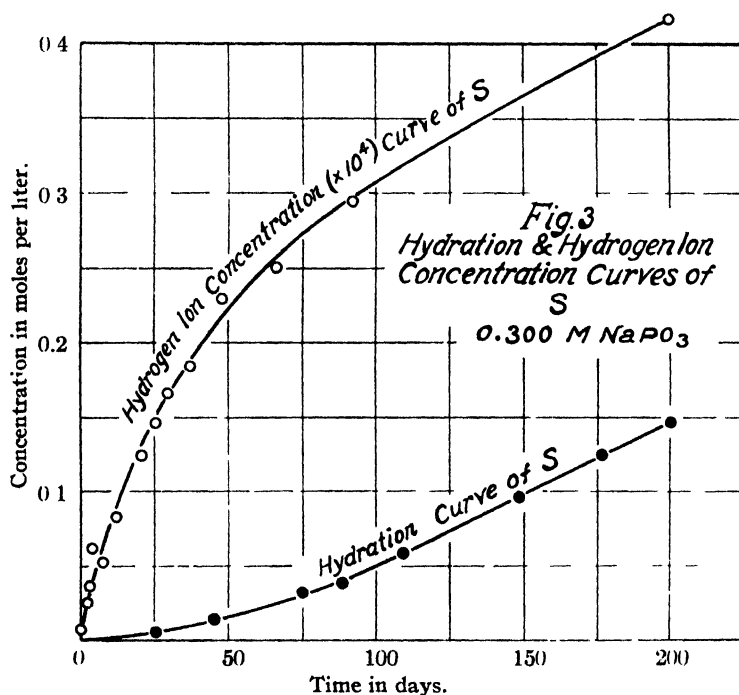
Fig. 2.—Hydration and hydrogen-ion concentration curves of solution Z, 0.300 M NaPO_3 , 0.010 M HCl.

more nearly completed. The explanation is obvious. Monometaphosphoric acid is a stronger acid than orthophosphoric acid. When, howev

there was no acid added to the solution, as in solution S, an actual increase in the concentration of hydrogen ion occurred. This increase was due to the formation of hydrogen ions during the reaction to pyrophosphate and orthophosphate in a region where the concentration of hydrogen was below that given by the solution of the end-product, monosodium orthophosphate.

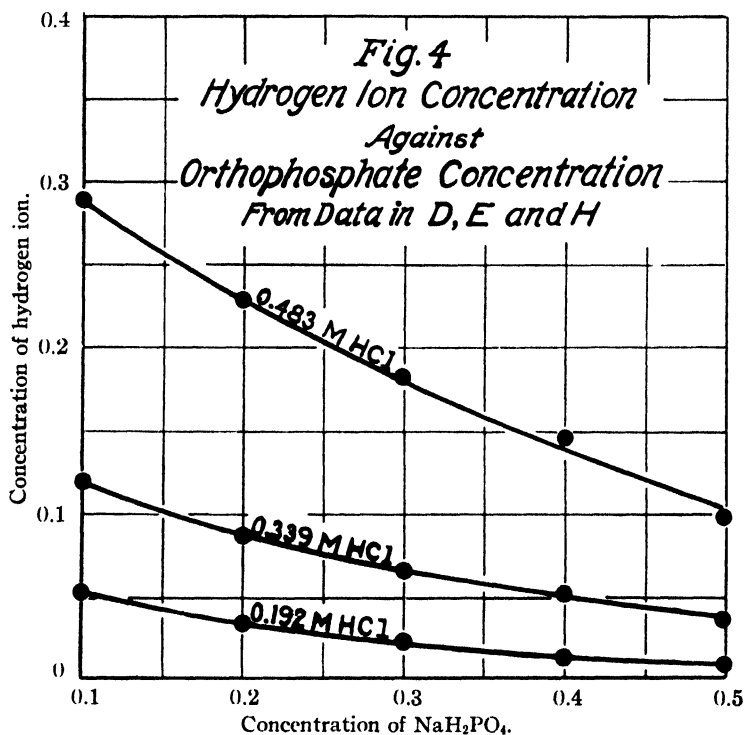
Abnormal Decrease of Hydrogen Ions in the First Part of Hydration.

In Figs. 1, 2, and 3, all the hydration curves show periods at the beginning where apparently very little orthophosphate was present in the solutions.



There was, however, at this point a reaction of a very pronounced character taking place. The hydrogen-ion concentration decreased more rapidly at this stage than at any other stage of its course. The change of hydrogen-ion concentration could not be explained by the very little orthophosphate which was undoubtedly present but not determinable. Even after the orthophosphate had acquired a comparatively high concentration it was insufficient to cause the change in concentration which occurred. For example, in Curve H, Fig. 1, there was a decrease of 0.14 mole of hydrogen ion when 0.10 mole of orthophosphate had been formed; in E, 0.13 mole, with the formation of 0.10 mole of orthophosphate; and in C, 0.16 mole of hydrogen ion disappeared when 0.10 mole of orthophosphate had been formed.

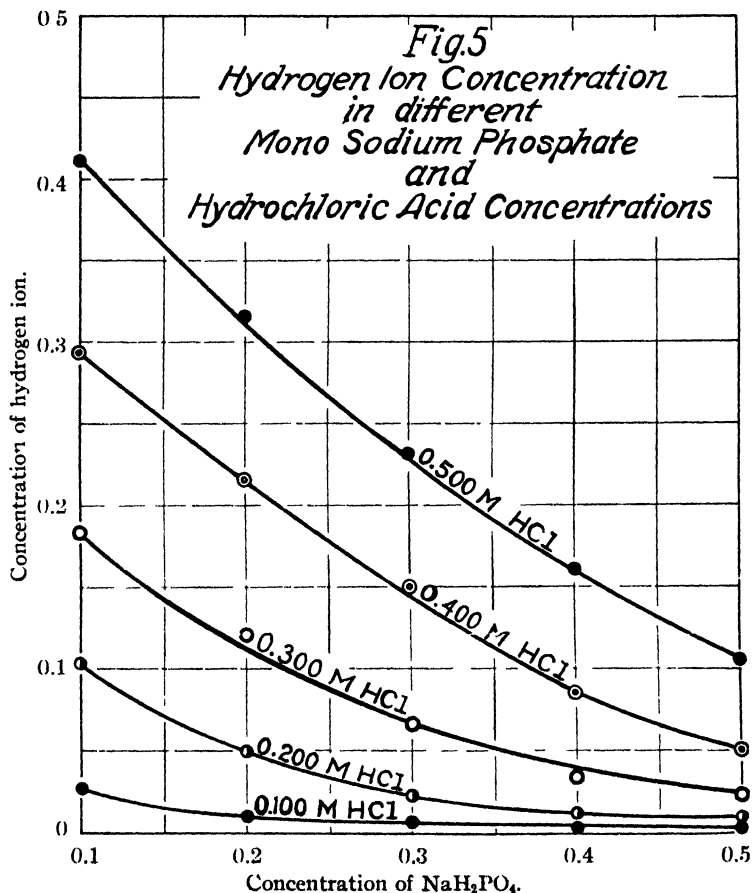
Furthermore, in studying these hydrations it was thought, at first, that the orthophosphate was produced directly from the metaphosphate. We therefore plotted the hydrogen-ion concentrations found against the orthophosphate concentration. These curves were compared with curves secured from the measurement of synthetic solutions of monosodium orthophosphate and hydrochloric acid in concentrations calculated to be identical with the experimental solutions, assuming that the orthophosphate was produced directly from the metaphosphate. It was thought proper to



omit the metaphosphate from these synthetic solutions since its effect on the hydrogen-ion concentration was slight. The curves in Fig. 4 represent the results from solutions D, E and H. Fig. 5 represents values from the corresponding synthetic solutions just described. When Fig. 5 is superimposed on Fig. 4 the result is shown in Fig. 6. The curves are not coincident. The hydrogen-ion values from the actual hydrations near the beginning are much lower than those from the seemingly comparable synthetic solutions. The differences, however, decrease as the reactions proceed, until finally, near completion, the concentrations of hydrogen ion in both cases become identical.

From the above consideration it is evident that synthetic solutions are

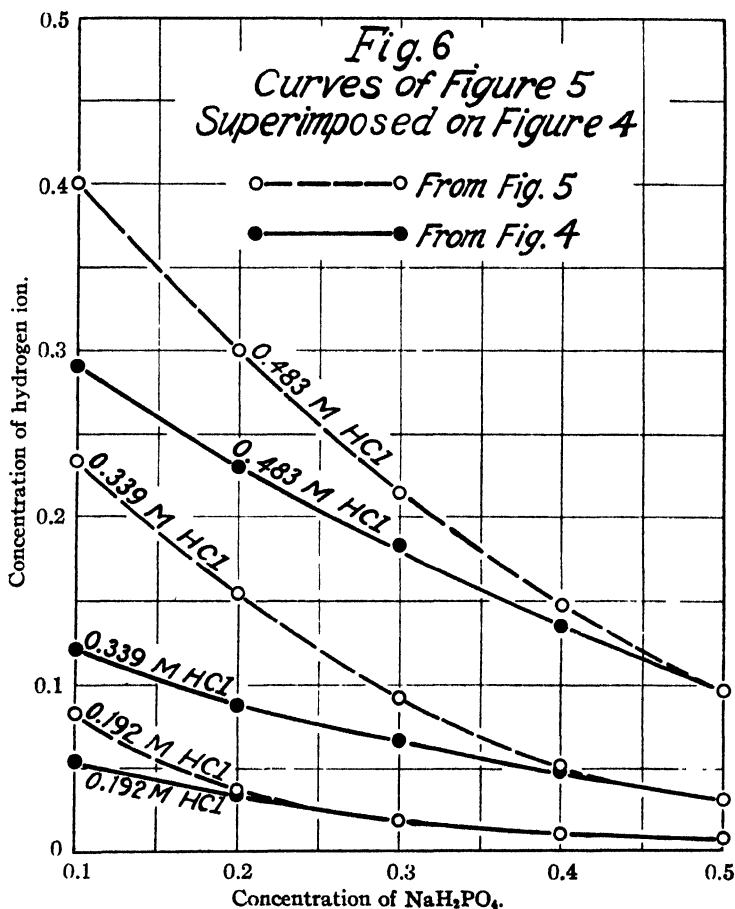
not entirely comparable to the solutions produced by hydrations. The actual solutions produced under conditions of hydration have a substance capable of diminishing the concentration of hydrogen ion beyond that which would be present if orthophosphate alone were formed. Therefore, inasmuch as pyrophosphate was detected during the analysis of samples and inasmuch as there was a decrease of hydrogen-ion concentration in



hydrochloric acid solutions when pyrophosphate is added, it seemed reasonably certain that the large decrease of hydrogen-ion concentration at the beginning was due to the pyrophosphate formed. During the reaction, however, it finally was hydrated to orthophosphate in the acid solution, thus tending to eliminate the difference of corresponding hydrogen-ion concentration values as the reaction approached more nearly complete transformation to orthophosphate.

In the hydration of solution S, where no acid was added, there was a

further indication of the formation of pyrophosphate. The concentration of hydrogen ion constantly increased. At the end of 200 days its value was 4.06×10^{-5} , while the concentration of 0.3 M monosodium phosphate, the natural end-product, gave a value of 3.81×10^{-5} . Then, too, the reaction was but 50 per cent. complete, with the hydrogen-ion concentration still showing a marked tendency to increase when judged



from the slope of its curve in Fig. 3. The final value it could ultimately attain would be about $1.5 \times 10^{-4}\text{ M}$, the value for a 0.15 M disodium dihydrogen pyrophosphate solution with no orthophosphate present. This concentration, moreover, could not be reached as orthophosphate was present. But the final value with no pyrophosphate present at complete transformation would be that for 0.300 M orthophosphate. Hence, a maximum in the hydrogen-ion concentration should be expected before complete hydration.

Comparison of Effects of Changes in Concentrations.—The results of the various hydrations indicate the comparative effects of the concentrations of metaphosphate and hydrochloric acid. The times required for the attainment of the same percentage transformation depended more upon the concentration of hydrogen ion in solution than upon the metaphosphate concentration. The data in Tables II, III, IV, V and VI, exemplified in Figs. 1, 2 and 3, confirm this assertion. Where the concentration of metaphosphate in solutions C, E and H initially was 0.500 *M*, with the hydrochloric acid 0.483 *M*, 0.339 *M* and 0.192 *M*, respectively, the times for the attainment of the same percentage hydration increased greatly with decrease of hydrogen-ion concentration. Likewise in solutions E, K and O, of 0.339 *M* hydrochloric acid and 0.500 *M*, 0.300 *M* and 0.100 *M* sodium metaphosphate, respectively, the concentration of hydrogen ion rather than the concentration of sodium monometaphosphate affects the rate of the reaction to the greatest extent. The influence of the concentration of hydrogen ion is most strikingly shown in solutions K, Z and S, of 0.300 *M* monometaphosphate with 0.339 *M*, 0.010 *M* and 0.000 *M* hydrochloric acid, respectively.

Summary

1. $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was prepared, a hydrate not hitherto described.
2. Sodium monometaphosphate was prepared and its hydration studied by direct methods.
3. The hydrogen-ion concentration decreased as the reaction proceeded in regions of initial concentration above that given by the end-product, monosodium orthophosphate, but increased when the initial hydrogen-ion concentration was below that of the end-product.
4. Pyrophosphate was formed as an intermediate product. Its presence was detected during the separation and determination of orthophosphate. The abnormally low values for the hydrogen-ion concentrations at the beginning with high hydrochloric acid concentrations and the increasing of the hydrogen-ion concentration above that of the final end-product indicated that an acid stronger than orthophosphoric but weaker than hydrochloric was formed.
5. The hydration was much more affected by a change of concentration of hydrogen ions than by a change of the concentration of sodium monometaphosphate.
6. The presence of an intermediate product makes the reaction somewhat complex.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF
HARVARD UNIVERSITY]

THE COMPRESSIBILITY OF TELLURIUM

BY ROBERT FRANKLIN MEHL¹ AND BEVERIDGE JAMES MAIR

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Although the cubic compressibilities of a large number of elements have been determined in the Harvard Chemical Laboratories during the last twenty-five years by Richards and his collaborators,² thus far tellurium has escaped attention.

Four years ago P. W. Bridgman, in the Jefferson Physical Laboratory, determined the linear compressibility of a single crystal of tellurium³ and discovered the surprising fact that an increase in hydrostatic pressure caused an increase in length along the axis under observation. In a later paper⁴ Bridgman redetermined this coefficient on a casting in which the axis measured corresponded closely to the trigonal axis, and also determined the linear compressibility coefficient perpendicular to this axis. These two values for initial linear compressibility at 30° are, respectively, -0.4137×10^{-6} and $+2.748 \times 10^{-6}$, leading to a positive value for the initial cubic compressibility at 30° of 5.082×10^{-6} , pressures always given in kg./cm.². Bridgman pointed out in this second paper that the value found for the initial cubic compressibility does not fall on the periodic compressibility curve of Richards⁵ when atomic weights are used, but does fall on a smooth curve through the values for the neighboring elements when atomic numbers are used.

In order to study further the remarkable behavior of this element it was thought advisable to make a direct determination of the cubic compressibility.⁶ A negative coefficient of cubic compressibility is of course contrary to ordinary ideas of pressure and its effects and indeed to the principle of Le Chatelier, but the case of a negative coefficient of linear compressibility is somewhat less clear. It will be shown that this negative coefficient is completely orthodox. The compressibility of tellurium, however, is interesting from another point of view. With iodine it constitutes one of the three pairs of elements showing a reversed order in the periodic table from that of the atomic weights. These exceptional

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² The results of most of these determinations have been given in a summary paper by T. W. Richards, *THIS JOURNAL*, **37**, 1643 (1915).

³ Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 5 (1923).

⁴ Bridgman, *ibid.*, **60**, 370 (1925).

⁵ Richards and others, *Carnegie Inst. Wash. Pub.*, **76**, 66 (1907).

⁶ Bridgman's second paper came to the authors' attention after the work reported here had been completed, and while there is overlapping to a small extent the point of view of the present paper is thought to be sufficiently distinct to merit a separate statement.

elements should serve to emphasize the dependence of compressibility upon the extra-nuclear electronic structure of the atom, that is, the compressibility values of the elements in these pairs should fall on a smoothly sloping curve through the values of the neighboring elements when plotted according to atomic numbers but not when plotted according to atomic weights. One of the remaining pairs, argon and potassium, is useless for the purpose since argon is a gas, and the other, nickel and cobalt, is of little use because the compressibilities of these two elements are nearly identical,⁷ falling upon a flat portion of the periodic curve of Richards. Tellurium, however, should fall upon a steeply rising portion of the curve, since tin and antimony on its left have coefficients of 1.9×10^{-6} and 2.4×10^{-6} , respectively, and iodine and cesium on its right (when atomic numbers are used) have coefficients of 13.0×10^{-6} and 61×10^{-6} (xenon, a gas, is of course omitted).⁸

Method

The methods used to determine the compressibility coefficient of tellurium and to standardize the piezometer with which the measurements were made have been described elsewhere in considerable detail⁹ and will not be given here. The measurements were made at 25° instead of the usual 20°, however, and it was necessary to determine a new correction factor for water to apply at this higher temperature.¹⁰ This factor could, of course, be calculated¹¹ but it was thought better to determine it directly, especially since a direct determination would provide a dependable value for the compressibility of water at 25°, a datum not hitherto available.¹²

The greatest difference between the amounts of water used in the de-

⁷ Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 5 (1923), found the compressibility coefficient of nickel to be 0.529×10^{-6} and that of cobalt 0.539×10^{-6} , both at 30°.

⁸ Richards, *This Journal*, **37**, 1643 (1915).

⁹ Richards, *J. Franklin Inst.*, **198**, 25 (1924); also Richards and Saerens, *This Journal*, **46**, 935 (1924).

¹⁰ Richards and Sameshima, *This Journal*, **42**, 49 (1920), used 0.2069 as the factor to be applied at 25°. This factor presumably was calculated from approximated values for the compressibility of water and that of mercury at 25°. The approximate nature of the factor used has no bearing upon the accuracy of the results obtained, since the amount of water used in each determination was nearly equal to that used in the standardization, so that the inaccuracy in the correction factor, appearing in the third decimal place, does not appear in the compressibility coefficients calculated. The compressibility coefficient for mercury at 25° used in the present work, namely, 4.00×10^{-6} , was taken from this previous paper.

¹¹ Richards, *Carnegie Inst. Wash. Pub.*, **76**, 33, 36 (1907).

¹² Amagat, *Ann. chim. phys.*, [6] **29**, 68, 505 (1893), determined the compressibility of water at 20° and 30° in intervals of 100 atm. between 100 and 500 atm. (and beyond). From these data an approximate value may be obtained for the average compressibility between 100 and 500 megabars and at 25°, namely, 41.9×10^{-6} . The value here determined directly is lower, and accurate to an additional decimal place.

terminations upon tellurium and that used in the standardization of the piezometer was 2.9993 g. A quantity of water roughly ten times as great was used for the determination of the water correction factor, in order to obtain a value sufficiently exact for the purpose without making a large number of determinations. Two experiments were carried out, yielding four values. These are given in Table I, together with the standardization factors of the piezometer used.

TABLE I

STANDARDIZATION OF PIEZOMETER

Wt. of water, 2.7928 g.

Wt. of mercury, 100-500 megabars.

0.7973 } .7966 } .7981 } .7985 }	0.8003 } .7931 } .7942 } .7908 }
.7938 } .8008 }	Average 0.7964 g. ^a

DETERMINATION OF WATER FACTOR

	Expt. No. 1	Expt. No. 2
Total wt. of water taken	26.8316 g.	27.1450 g.
Total wts. of mercury, 100-500 megabars.....	5.712 } 5.720 } g.	5.764 } 5.780 } g.
Wt. of mercury, 100-500 megabars, in excess of that used in standardization.....	4.916 } 4.924 } g.	4.968 } 4.984 } g.
Wt. of water in excess of that used in standardization.....	24.0388 g.	24.3522 g.
Water factor: wt. of mercury, 100-500 megabars per 1 g. of water.....	$\frac{4.916}{24.039} = 0.2045$ $\frac{4.924}{24.039} = 0.2048$	$\frac{4.918}{24.352} = 0.2040$ $\frac{4.984}{24.352} = 0.2044$
	Average: 0.2044	

^a These values refer to a common quantity of water, namely, 2.7928 g., and have been found by converting the original values to this basis by applying the water correction factor for the difference. The bracketed values represent the pairs obtained from single standardizations.

The compressibility of water may be calculated from the above data in the usual way, after correction is made for the air displaced by the weight of water in excess of that used in the standardization.¹³ The four determinations yield values for $\beta_{\text{H}_2\text{O}, 25^\circ}$ of 41.55×10^{-6} , 41.60×10^{-6} , 41.45×10^{-6} , and 41.57×10^{-6} , with an average value of 41.54×10^{-6} .

¹³ The water correction factor is applied to differences of water as weighed in air and no correction for air displacement during weighing is necessary, but, since compressibility refers to true volume, appropriate correction for the air displaced by the water and the weights must be made.

Materials

Tellurium: An analysis showed 99.98% of tellurium;¹⁴ no attempt was made to determine the nature of the impurity present since it is known that impurities in such quantities have a negligible effect upon compressibility with the order of accuracy now attainable.

In order to eliminate voids as much as possible the tellurium was remelted in a Pyrex tube and cast in such a way as to form a single crystal.¹⁵ The tube was chosen of such a size that the casting obtained fitted closely to the piezometer barrel, in order that the quantity of water might be kept at a minimum. The castings obtained, length 22.0 cm. and diameter 1.5 cm., were beautifully crystalline, showing a series of parallel plane markings along which the crystal tended to crack, inclined steeply to the longitudinal axis.

The density was determined upon fragments of the crystal after the compressibility determinations had been made. The usual water displacement method was used with especial care to have possible fissures filled with water. This was done by first immersing the fragments in a large tube nearly filled with water and evacuating the free space. Under this treatment the air held by the crystal greatly expanded, and it became an easy matter to remove the bubbles formed. The crystals were then promptly transferred to a vessel of water in which they were to be weighed. Three determinations upon different pieces gave values for the density of tellurium of 6.258, 6.262, 6.262, average, 6.261, correction having been made for displacement of air.¹⁶

Determination of Compressibility

The compressibility data are given in Table II.

TABLE II
COMPRESSIBILITY DATA

Wt. of unicrystalline casting: 133.514 g.

Piezometer constant: 0.7964 g. mercury with 2.7928 g. water.

Amt. of water used	Mercury, 100-500 megabars	$\beta \times 10^4$	Av. values
5.5652	1.4796 } 1.4796 }	5.01 } 5.01 }	5.01
5.7707	1.5210 } 1.5234 }	5.00 } 5.02 }	5.01
5.7921	1.5189 } 1.5300 }	4.95 } 5.04 }	5.00
5.8692	1.3363 } 1.3363 }	5.00 } 5.00 }	5.00
3.9670	1.1486 } 1.1667 }	4.89 } 5.04 }	4.97
4.2473	1.2222 } 1.2213 }	5.02 } 5.02 }	5.02

¹⁴ This material was very kindly furnished by Mr. Willis T. Burns, manager of the Raritan Copper Works, Perth Amboy, New Jersey. It had been refined from a cruder sample containing 1% of selenium.

¹⁵ The technique used by Bridgman, Ref. 3, was used here without modification.

¹⁶ Kahlbaum, *Z. anorg. Chem.*, 29, 289 (1902), found 6.235, and Beljankin, *J. Russ. Phys. Chem. Soc.*, 33, 670 (1901), found 6.338.

The figures here given have their usual significance. Each experiment yielded two (bracketed) figures, the first representing the descent from 500 to 100 megabars and the second the ascent from 100 to 500 megabars made without refilling. It was thought better to start at the higher pressure in order to set the stopper more firmly and quickly, for any progressive settling would cause a lack of coincidence between the two legs of the pressure-volume curve. The correspondence between the members of each pair of figures illustrates the reproducibility of the method, but comparison between separate determinations should be made with the average value for each pair. This is done in the last column of the table, and the agreement between the average values may be seen to be very close.

After a number of determinations had been made the tellurium was remelted and recast, and additional determinations were made in order to free the measurements from any suspicion of error occasioned by imperfections in the original casting. These are the last two determinations in Table II, and they agree with the preceding values within the limit of accuracy, though the first is probably somewhat low.

The average of these six determinations, 5.00×10^{-6} , which represents the average compressibility between 100 and 500 megabars, is probably accurate to within two in the second decimal place.¹⁷

Discussion

Fig. 1 shows that the value here determined for the compressibility of tellurium fits nicely upon a smooth curve through the corresponding values for tin, antimony, iodine and cesium when the elements are plotted along the abscissa according to atomic numbers, and that the order of the compressibility coefficients is the same as that of the atomic volumes.¹⁸

¹⁷ The value calculated by Bridgman from the linear compressibilities parallel to the trigonal axis and perpendicular to it, 5.082×10^{-6} , represents the initial compressibility at 30°, pressure taken in kg./cm.². This can be transformed to a value representing the average compressibility between 100 and 500 megabars at 25° by correcting for the difference in temperature, the difference in pressure units and the difference in pressure range. The first two corrections will tend to increase Bridgman's value, since the compressibility has been found to increase with falling temperature, and since the volume change per megabar is greater than per kg./cm.², but the third correction tends to decrease it, since the compressibility here decreases with increasing pressure. The corrected value is 5.12×10^{-6} , and is appreciably higher than the value determined here. Bridgman does not state how closely the axis measured corresponded to the true trigonal axis; a small variation would be sufficient to account for the discrepancy, since the coefficients for the two axes are so greatly different.

It would appear, therefore, that Richards' method is simpler for the determination of volume compressibility, since no attention need be paid to crystallographic orientation, though for this reason it furnishes no information whatever concerning compressibility anisotropy.

¹⁸ The atomic volumes have been calculated from the density data given in the International Critical Tables, Vol. I, page 103.

It is evident, therefore, that the mass of the nucleus has, so far as these measurements can show, a negligible effect upon compressibility. With the interpretation of the other periodic properties upon the basis of the extra-nuclear atom following the work of Moseley, compressibility, shown by Richards to be a periodic function, likewise received the common explanation. The significance of the present work, therefore, is chiefly one of emphasis and confirmation.

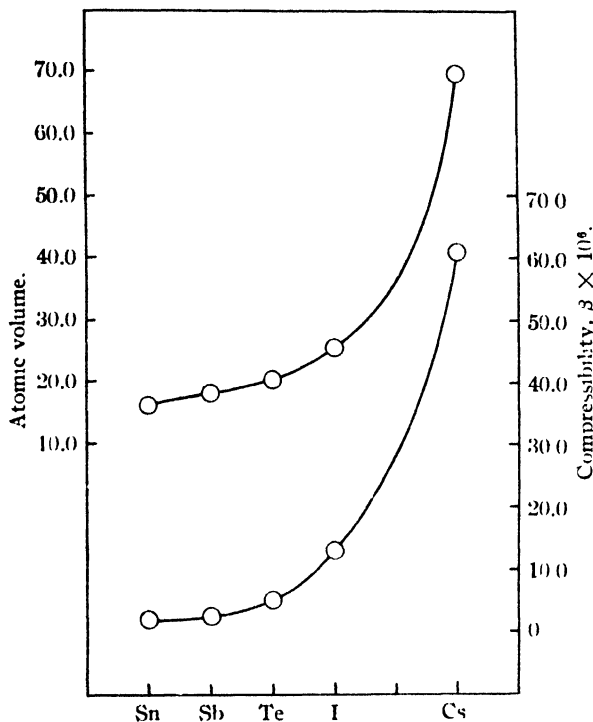


Fig. 1

Analysis of the curve given in Fig. 1 is beyond hope at present, and will probably not be made until the positions of the electronic orbits in each element and the interaction of the electrons, and also the directive interatomic forces, related to the crystal structure, are understood.

There now remains only to explain the remarkable negative coefficient of linear compressibility found by Bridgman. This effect was observed for tellurium alone, and Bridgman attempted no explanation.

The crystal structure of tellurium is well known.¹⁹ The atoms are arranged on a triangular lattice, the side of the unit basal triangle, a , measuring 4.445 Å., and the height of the unit prism, h , 5.912 Å. The

¹⁹ Slattery, *Phys. Rev.*, [2] **21**, 378 (1923). Bradley, *Phil. Mag.*, **48**, 477 (1924).

density of the element requires three tellurium atoms associated with each lattice point. These atoms are arranged around the prism edge to form an ascending helix, with a threefold symmetry, each atom exactly above the third atom below in the same helix; the prism edge is thus a screw-axis. The intersections of the axes of these helices with the basal plane form the unit basal triangles. This is the Sohncke point-system 23 or 24, the x-ray method being unable to make a decision between the two systems, which differ only in the direction of the screw. For the purposes of the demonstration given here it is immaterial whether the screw is right-handed or left-handed. The radius of the helix can be calculated from Bradley's data, and is 1.20 Å., representing the distance from the center of each atom to the axis of the helix.

There are thus two inter-atomic distances, namely, that between atoms in the same helix and that between atoms in different helices. As Bradley showed for selenium it may be shown for tellurium also that the distance between nearest atom centers in the same helix is much less than that between atom centers in different helices. For tellurium these values are 2.86 Å. and 3.46 Å., respectively. This doubtless means that the atoms in the same helix are held together by cohesive forces much greater than those binding atoms in different helices, and that the crystal is "harder" in the direction of the screw-axis than perpendicular to it. Bradley has pointed out that the uniqueness of this axis, present in both selenium and tellurium, doubtless accounts for many of the directional properties observed in the two elements, and that crystallization is probably preferentially along this axis. This was found to be the case by Bridgman, who states that the trigonal (screw) axis lay longitudinally in the casting.

It is evident that this crystal structure is not closely packed, and it is conceivable that a change in either of the major dimensions, that of the side of the unit basal triangle, a , or that of the prism edge, h , should cause a change in density resulting merely from a difference in the closeness of the packing of the atoms, the two inter-atomic distances remaining unchanged. In such a process a lengthening of the prism edge h would cause a shortening of a and also a shortening of the radius of the helix. If such an elongation would result in an increase in density, it is entirely reasonable to suppose that an increase in pressure, tending towards an increase in density, would in fact cause a lengthening of this axis, with an attendant shortening of the other two dimensions. Such a lengthening would obviously cause the abnormal coefficient observed by Bridgman.

Fig. 2 shows a curve representing density as a function of the height of the unit prism. The values from which the curve was plotted were calculated by taking a series of values for h and keeping the inter-atomic distances, 2.86 Å. and 3.46 Å., unchanged, calculating the radius of the

helix and the side of the unit basal triangle, a , and from these the density of the hypothetical crystal. The curve passes through a minimum at a density slightly greater than 6.20, corresponding to a value for h of 5.55 Å. For a prism of height less than 5.55 Å. an increase in pressure tending to cause an increase in density could do so only by shortening h , the two interatomic distances remaining unchanged, and the screw-axis would therefore show the usual positive compressibility coefficient. On the other hand, if the value for h lay to the right of 5.55 Å. an increase in pressure would cause a lengthening in h , since such a process would result in an increase in density. The actual value of h for tellurium, indicated by the arrow in the figure, is 5.91 Å. and is therefore to the right of the minimum, so that an increase in pressure should cause an increase in h , or, in other words, a negative compressibility coefficient along this axis.

Apparently no measurements have been made upon the compressibility of selenium along the screw-axis, but on the basis of the reasoning advanced here its behavior can be predicted. Fig. 3 is a curve for selenium similar to Fig. 2 for tellurium. The actual value for

h , indicated by the arrow, appears to lie very slightly to the left of the minimum, and therefore the height of the unit prism would very likely decrease with the application of pressure (assuming, of course, that the lattice dimensions used in the calculations are correct); but since the screw-axis is in a state of greater compression than the triangular axes the compressibility along this axis is probably low.

Resisting the elongation (or contraction) of the helix upon the application of pressure, there is the tendency within the lattice to maintain the angle formed by any three atoms in the same helix at (for tellurium) 126.5° , and this tendency doubtless becomes more and more urgent as the angle departs further and further from this value, so that it may be assumed that the adjustment of density by the lengthening or shortening of the helix meets with increasing resistance as the pressure rises. It

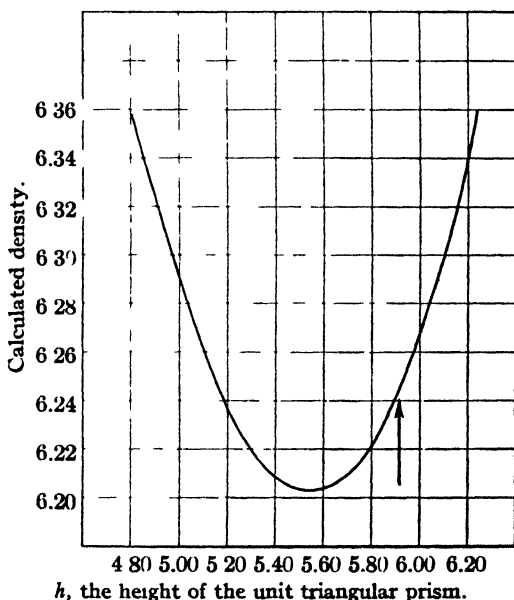
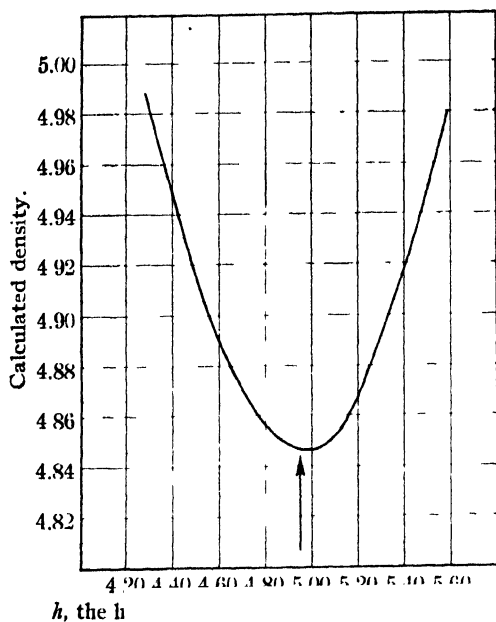


Fig. 2.—Tellurium.

is this restraint which prevents the helix from straightening completely upon the first application of pressure.



It is wholly possible, if the reasoning advanced here is valid, that other substances might be found to show negative coefficients of linear compressibility when the crystal structure permits an adjustment of packing similar to that in the case of tellurium. Structures such as those represented by the Sohncke point-systems 19 and 20, and 23 and 24, that is, possessing a screw-axis, should show this behavior when h is on the right (or left) of the minimum, though when the substance concerned is a chemical compound it is probable that the directive forces, presumably

here much stronger than in the elementary state, might offer much greater resistance to the elongation of the screw-axis.

In conclusion the authors wish to express their indebtedness to Professor F. W. Richards for the use of the apparatus and also for the kindly interest he has taken in the work.

Summary

1. The average cubic compressibility of tellurium between 100 and 500 megabars and at 25° has been found to be 5.00×10^{-6} , the significance of this result has been discussed.

2. An approximate value has been found for the compressibility of water at 25° , namely, 41.54×10^{-6} .

3. The negative coefficient of linear compressibility observed by P. W. Bridgman has been explained and a prediction made concerning the behavior of selenium. It is pointed out that a negative linear compressibility is not denied by the principle of Le Chatelier and that under certain conditions might be observed in other substances.

THE FREE ENERGY OF FORMATION OF PHOSPHINE

BY DAVID H. DRUMMOND

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The elements that stand in the group between metals and non-metals have been studied very little from the standpoint of thermodynamics. Before 1923, no systematic study of the free energy of the compounds of silicon, phosphorus, boron, arsenic, antimony, tellurium and selenium had been made. The purpose of this investigation was to determine the free energy of formation of phosphine by the measurement of the thermal dissociation of the gas.

Experimental Part

Some preliminary experiments were made to determine the thermal decomposition of phosphine. It seemed probable that phosphine would decompose at low temperatures, since its homologs, arsine and stibine, do so. Some phosphine was passed through a glass tube which was heated near the center for a few minutes. The phosphine was then washed out with carbon dioxide and the ends of the tube closed off. When the tube was opened in a dark room a bright phosphorescence was apparent beyond the point where the tube had been heated. The gas is decomposed by heat and the phosphorus is condensed before it can recombine with the hydrogen.

If the temperature is kept slightly above the boiling point of phosphorus, equilibrium will result. If the gas is cooled quickly the phosphorus will condense before the recombination will have time to take place. The free energy of phosphine can, therefore, be determined by quickly cooling the gas after it has been heated and then determining the ratio of hydrogen to undecomposed phosphine.

The apparatus for the measurements consisted of a glass tube, enclosed in a muffle, through which dry phosphine was passed. The tube extended into a water-bath. On the end of the tube a potash bulb was placed, containing a saturated solution of copper sulfate. This tube absorbed the phosphine. The hydrogen was mixed with dry air at a T-joint and then passed through hot platinized asbestos. The water formed was

TABLE I

DEGREE OF DECOMPOSITION OF PHOSPHINE					
ΔPH_3 , mg.	ΔH_2O , mg.	T , °C.	$\ln K$	I^a	P , atm.
20.0	12.15	573	1.061	2.59	0.811
38.6	31.5	583	0.718	2.72	.812
17.6	19.9	593	.438	2.52	.811
28.15	32.45	603	.344	2.31	.812
21.0	25.85	613	.182	2.16	.812
35.15	27.05	578	.765	2.82	.825
6.9	7.45	608	.252	2.58	.855

^a Mean value of I , 2.52.

absorbed in a calcium chloride tube. The temperature was controlled by hand to $\pm 1^\circ$. Table I shows the results of these experiments.

Discussion

Solid white phosphorus at a temperature of 25° is the standard reference state for phosphorus. Since the measurements were made in the gaseous phase the free energy of fusion and vaporization must be known to calculate the standard free energy of formation.

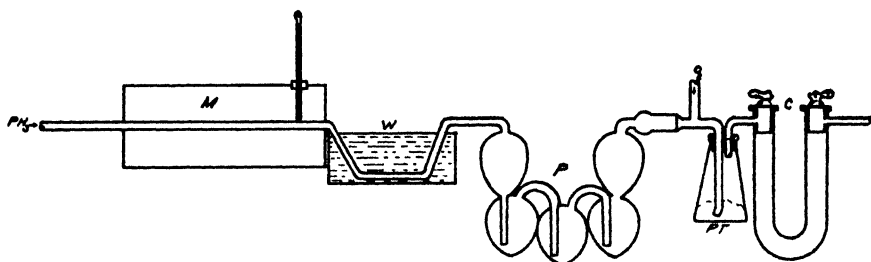


Fig. 1. - Diagram of apparatus. M, muffle; W, water bath; P, copper sulfate bulbs; P. T., platinized asbestos; C, drying tube.

The heat capacity of phosphorus as given by Richards and Jackson is 5.24 from 85°K. to 293°K. The value 5.4 at 298°K. is given by Kopp. Equation (1) fits these data fairly well.

$$C_p(P_s) = 5.30 + 0.000341T \quad (1)$$

Because of lack of data it is necessary to assume that the law of Dulong and Petit holds for fused phosphorus. This is probably very near the truth since there is an increase in heat capacity after fusion. The heat capacity equation for fused phosphorus is

$$C_p(P_l) = 6.10 + 0.000341T \quad (2)$$

Using the value 160.0 cal. for the heat of fusion of phosphorus¹ the equation for the free energy of fusion is

$$\Delta F = -70 - 0.8T \ln T + 4.87T \quad (3)$$

For the standard free energy change in fusion this gives the value 13.1 cal.

Taking 12,600 cal.² for the heat of vaporization of phosphorus, and using the heat capacity equation for a quadri-atomic gas³ the general free-energy equation for vaporization is

$$\Delta F^\circ(4P_l, P_g) = 58,871.7 + 15.4T \ln T + 0.00033T^2 - 0.0000008T^3 - 203.7T \quad (4)$$

Equation (4) gives 6063 cal. for the standard free energy of vaporization of one gram atom of phosphorus. The entropy change in fusion and

¹ Landolt and Börnstein, "Tabellen," p. 1468.

² *Ibid.*, p. 1475.

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 80.

vaporization can be calculated from the free-energy equation. The value 0.506 is obtained for the entropy change in fusion. The entropy change in vaporization is 25.5. Lewis and Randall⁴ give for the entropy of phosphorus gas the value 35.95. Subtracting the entropy changes of vaporization and fusion, the value 9.95 entropy units is found for the standard entropy of phosphorus.

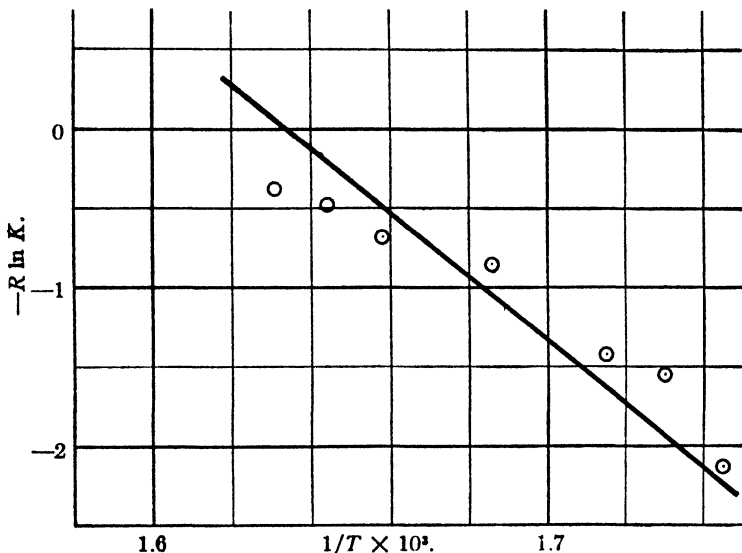
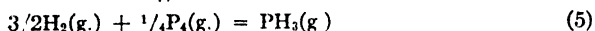


Fig. 2.

Taking -4900 cal.^5 as the standard heat of formation of phosphine, and subtracting the heats of vaporization and fusion, the value $-17,660.5 \text{ cal.}$ is obtained for the heat change in the reaction:



Using the heat-capacity equations³ for the gases involved in the reaction, the general free energy equation is

$$\Delta F^\circ = -16,486.5 + 3.72T \ln T + 0.0004T^2 + 0.0000007T^3 + IT \quad (6)$$

The values of $\ln K$ given in Table I are calculated from equation (7) upon the assumption that the partial pressures of the gases are proportional to their mole fraction.

$$\Delta F^\circ = -RT \ln \frac{P_{\text{PH}_3}}{(P_{\text{H}_2})^{3/2} (P_{\text{P}_4})^{1/4}} = -RT \ln K \quad (7)$$

The mean value of I , as shown in Table I, is 2.52. The free energy of formation of phosphine from hydrogen and solid phosphorus at 298°K. , as calculated from equations (3), (4) and (6), is -3296.0 cal.

The entropy change in the reaction as calculated from the free energy

⁴ Ref. 3, p. 464.

⁵ Ref. 1, p. 1491.

equation is -27.72 . This value gives for the standard entropy of phosphine the value 52.4 entropy units.

If $-R \ln K$ is plotted against $1/T$, the slope of the curve is ΔH . This was done on a large scale plot between the limits 573°K. and 613°K. The points were somewhat scattered. A line drawn through the means of these points had a slope of $-20,200$ as compared with the value $-19,711$ cal., calculated from the equation for the heat of reaction.

In conclusion the author wishes to thank Dr. R. K. McAlpine for his kind help and encouragement in this investigation. Acknowledgment is also due to Mr. L. D. Anderson of the Riverton High School for his kindness in lending some of the apparatus used in these experiments.

Summary

1. The equations have been worked out for the free-energy change of fusion and vaporization of white phosphorus. The standard free energies of these changes have been calculated.

2. The dissociation of phosphine has been measured in the temperature interval 573°K. to 613°K. From this the free energy of formation of phosphine has been calculated.

3. The entropy change of vaporization and fusion and the standard entropy of phosphorus have been calculated. The standard entropy of phosphine has been calculated.

RIVERTON, WYOMING

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MACDONALD COLLEGE]

DISSOCIATION PRESSURES OF AMMONIUM ORTHOPHOSPHATES¹

By T. E. WARREN

RECEIVED APRIL 28, 1927

PUBLISHED AUGUST 5, 1927

Recent developments in the manufacture of ammonia² and phosphoric acid³ have demonstrated the possibility of the commercial use of ammonium phosphate as a fertilizer. As such it contains two of the fundamental plant nutrients in readily available form.⁴

The most economical starting state for ammonia is the gaseous and for phosphoric acid a concentrated solution, the latter because the heat of reaction is sufficient to dry the product. The various reactions of ammonia gas with phosphoric acid have been the subject of the following experiments made by the author.

¹ From a thesis submitted in partial fulfillment of the requirements for the degree of M. Sc. in McGill University.

² Brown, *Trans. Am. Electrochem. Soc.*, **48**, 175-182 (1925)

³ Jacob, *ibid.*, **48**, 125-133 (1925).

⁴ Allison *Soil Science*, **5**, 1-80 (1918).

Knowing the dissociation pressures of ammonia over saturated solutions of mono- and di-ammonium phosphates it is possible to prepare a gas mixture with a partial pressure of ammonia lying between these values. By passing this mixture into phosphoric acid, mono-ammonium phosphate can be formed without producing any di-ammonium phosphate, even though the passage of gas is continued after all of the free phosphoric acid has been neutralized. A similar process is, of course, applicable to the manufacture of the di- and tribasic salts in the pure, dry state.

Mono-ammonium phosphate crystals made by the rapid neutralization of concentrated phosphoric acid contain hygroscopic, occluded acid. This may be neutralized without the formation of di-ammonium phosphate by drying with an air-ammonia mixture as mentioned above.

Since mono-, di- and tri-ammonium phosphates are made by the precipitation of the salts from saturated solutions, concentration is not a variable. Accordingly, the dissociation pressures were determined with the dry, powdered salts which, from thermodynamic reasoning, must have the same dissociation pressures as the saturated solutions. The temperature range of the measurements, 80–125°, was chosen to include the zone of precipitation and drying.

Materials

The mono-ammonium phosphate used in the determination of the dissociation pressure was Merck's c. p. This salt in solution was slightly acid to methyl red and was heated for several hours before using to dissociate any di-ammonium phosphate which may have been present. In this connection the author was misled by a preliminary experiment made with Kahlbaum's c. p. mono-ammonium phosphate which contained some of the secondary salt and in solution was neutral to methyl red.

The di-ammonium phosphate used in the measurements was Baker's c. p. It contained none of the tribasic salt.

No attempt was made to dry the two salts completely because moisture does not interfere with the air-saturation method of vapor pressure determinations.

Experimental

Measurements of the partial pressure of ammonia over mono- and di-ammonium phosphates were made with a type of air-saturation apparatus. A measured amount of air was passed at a uniform rate through a purifying train of soda lime and phosphorus pentoxide and thence to a constant-temperature well containing alternate layers of the finely powdered salt and glass wool. The gas then bubbled through an absorbing worm containing an excess of standard sulfuric acid. At the end of the run the excess acid was titrated and the partial pressure of ammonia calculated. The constant-temperature well was vapor-jacketed and benzene, water, toluene,

n-butyl alcohol and amyl alcohol were used for heating. The temperature could be controlled to 0.02° for the duration of a determination (about 2 hours) and the powder within the well was uniformly heated to the boiling point of the heating liquid. That equilibrium was reached was proved by making several runs at different rates for each temperature.

At 100° mono-ammonium phosphate had so small a dissociation pressure that it could not be measured, and even at 125° the pressure was only 0.05 mm.

The results of the di-ammonium phosphate experiments are shown in Table I.

TABLE I
DISSOCIATION PRESSURE OF DI-AMMONIUM PHOSPHATE

Temp., $^\circ\text{C}$.	1/Abs. temp.	Dissoc. press., mm. Hg.
80.24	0.002830	1.36
99.91	.002680	5.02
109.30	.002615	11.00
116.89	.002564	17.74
125.36	.002509	29.35

A plot of the logarithm of the dissociation pressures of di-ammonium phosphate against the reciprocals of the corresponding absolute tem-

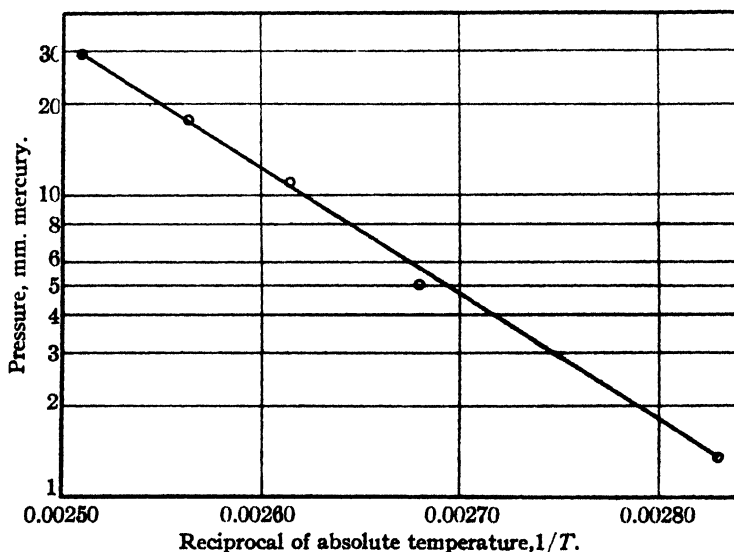
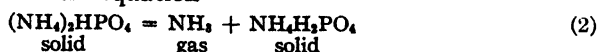


Fig. 1.—Dissociation pressures of ammonium phosphate.

peratures is given in Fig. 1. Substituting values from the straight line of Fig. 1 in the equation

$$(\ln K_1 - \ln K_2) = \frac{DH}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1)$$

the heat of reaction for the equation



is found to be 19,050 calories.

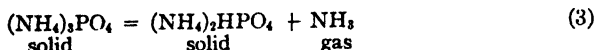
From Kopp's⁵ law the molal heat capacity of ammonia in a solid is 13.3 calories per mole, while in the gas phase⁶ it is given by the equation $8.04 - 0.0007T + 0.0000051T^2$. Hence the molal heat capacity of the products of equation (2) at 373°K. is $13.3 - 9.1 = 4.3$ calories less than that of reacting substances, and the heat of reaction is $4.3 \times 45 = 194$ calories greater at 80° than at 125°. Since this would make the curve in Fig. 1 concave to the origin, with a curvature of 1 per cent., the experimental values for four of the points are in nice agreement. The point corresponding to 100° lies below the curve and the discrepancy is not within the limit of experimental error. The standard solutions, volumetric apparatus and thermometers were used in the other measurements and carefully evaluated and the point is the arithmetic mean of six separate determinations, of which none varies more than 2 per cent. of its value from the mean

The dissociation pressure of tri-ammonium phosphate was too great to measure in the air-saturation apparatus so the determinations were made by the static method. They are less accurate than those of the di-ammonium phosphate because of difficulties introduced by water formation, possibly from the production of some metaphosphate at high temperatures, and slowness of absorption at pressures lower than atmospheric.

Since dry tri-ammonium phosphate was not purchasable, it was prepared from the dibasic salt in the apparatus itself by passing ammonia at 100° and 1 atmosphere pressure over it. The tube containing the dry tri-ammonium phosphate was then attached through a mercury seal to a mercury manometer and a current of pure dry ammonia gas bubbled over it and through the manometer. When the salt and the apparatus were dry and free from any foreign gas the tube was sealed off at a constriction.

Because of the prementioned difficulty of slow absorption, only points near or above atmospheric pressure were determined, and such lower values as were needed were found by extrapolation.

The values obtained are given in Table II. In view of their small number their accuracy justifies only an approximate calculation of the heat of reaction. Calculated as before, its value is 9400 calories for the reaction



⁵ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, 1923, p. 77 [$6.4 + 3(2.3) = 13.3$].

⁶ *Ibid.*, p. 80.

TABLE II
DISSOCIATION PRESSURES OF TRI-AMMONIUM PHOSPHATE

Temp., °C.	Dissoc. press., mm. Hg
110.1	733.1
116.5	825.7
125	1177

To check the vapor-pressure determinations, pure mono-ammonium phosphate was prepared by passing a large excess of a 1 per cent. ammonia-air mixture through concentrated phosphoric acid at 110°. The product had a dissociation pressure of ammonia corresponding to mono-ammonium phosphate and in solution at 110° would absorb no ammonia from the 1 per cent. mixture. A product having the dissociation pressure of di-ammonium phosphate was obtained by lowering the temperature to 100° while the 1 per cent. mixture was passed through. Pure, dry tri-ammonium phosphate was made by treating di-ammonium phosphate at 100° with ammonia at 1 atmosphere pressure.

The writer wishes to thank Dr. Milton Hersey of Montreal for a scholarship which rendered the research possible and Dr. J. F. Snell for supervision and for the facilities afforded in Macdonald College.

Summary

The reactions of gaseous ammonia and phosphoric acid solutions have been studied in order to produce the three ammonium salts of phosphoric acid in a pure state.

To produce the desired salt with the exclusion of the others, a variation in the partial pressure of the ammonia gas was used. This necessitated the determination of the dissociation pressures of mono-, di- and tri-ammonium phosphates. The pressure of mono-ammonium phosphate over the range 80–125° was less than 0.05 mm.; that of di-ammonium phosphate was 1.4 mm. at 80° and 30 mm. at 125°. The partial pressure of tri-ammonium phosphate, determined less accurately, was 730 mm. at 110° and 1170 mm. at 125°.

Using the partial-pressure method, pure mono-, di- and tri-ammonium phosphates were prepared.

QUEBEC, CANADA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES BUREAU OF SOILS]

THE HEAT OF FORMATION OF AMMONIUM CARBAMATE FROM AMMONIA AND CARBON DIOXIDE

BY K. G. CLARK AND H. C. HETHERINGTON

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In the synthesis of urea from ammonia and carbon dioxide, the two reactants first combine to form ammonium carbamate as follows, $2 \text{NH}_3 + \text{CO}_2 \rightarrow (\text{NH}_3)_2\text{CO}_2$, with the liberation of a considerable quantity of heat. The present study was undertaken with the object of obtaining an accurate measure of this heat for use in such connections as the design and control of urea synthesis apparatus. Experimental determinations of this value have previously been made,^{1,2} and in addition there are available vapor-pressure data³ from which a value may be calculated, but examination of this material revealed discrepancies which would impair its usefulness.

The experimentally determined values range from 37,700 cal. to over 42,000 cal. per mole at constant pressure. An even wider variation is encountered as shown in Table I, when the heat evolved at constant volume is calculated from existing vapor-pressure data by means of the van't Hoff equation.

TABLE I
CALCULATED HEAT OF REACTION

Temp range, °C.	cal /g. mole		Source of vapor-pressure data
	Maximum	Minimum	
10.0- 30.0	36,670	36,200	Naumann ^{3a}
14.9- 30.0	39,510	32,290	Briggs ^{3g}
30.0- 50.0	39,170	38,510	Naumann ^{3a}
30.9- 44.9	38,280	36,660	Briggs ^{3g}
37.8- 49.6	35,540	31,710	Isambert ^{3c}
49.6- 67.6	40,350	31,750	Isambert ^{3c}
50.0- 60.0	38,460	30,820	Naumann ^{3a}
77.2-114.5	45,450	37,740	Briner ^{3e}
114.5-152.0	42,660	36,270	Briner ^{3e}
152.0-197.0	46,090	22,910	Briner ^{3e}

It will be seen that at temperatures above 30° the results become very erratic. This is no doubt due in the first place to the difficulties in making accurate pressure determinations at elevated temperatures,

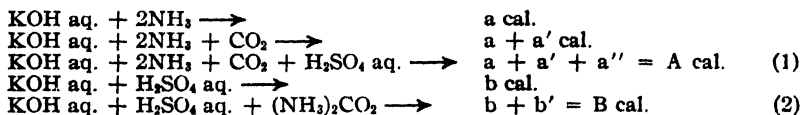
¹ Raabe, *Rec. trav. chim.*, **1**, 158 (1882).

² Matignon, *Ann. chim. phys.*, [8] **14**, 24 (1908).

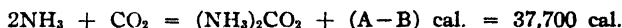
³ (a) Naumann, *Ann.*, **160**, 15 (1871). (b) Horstmann, *Ann.*, **187**, 48 (1877). (c) Isambert, *Compt. rend.*, **92**, 919 (1881); **93**, 731 (1881); **94**, 958 (1882). (d) Engel and Mortessier, *ibid.*, **93**, 595, 899 (1881). (e) Briner, *J. chim. phys.*, **4**, 266 (1906). (f) Fichter and Becker, *Ber.*, **44**, 3473 (1911). (g) Briggs and Migrdichian, *J. Phys. Chem.*, **28**, 1121 (1924).

and at the pressures encountered in the case of ammonium carbamate; secondly, to the tendency of the reaction $(\text{NH}_3)_2\text{CO}_2 \rightarrow (\text{NH}_3)_2\text{CO} + \text{H}_2\text{O}$ to take place during the time required for vapor-pressure measurements. Finally, the unknown extent of the variation from the perfect gas laws of a mixture of ammonia and carbon dioxide renders the data for the higher pressures untrustworthy.

Previous Experimental Methods.—Lecher⁴ determined the heat evolved in ammonium carbamate formation by determining heats of solution and heats of neutralization, obtaining 37,700 cal. at constant pressure, as follows:



Combining Reactions 1 and 2



Raabe¹ employed the direct method at one atmosphere, using a continuous flow of ammonia and carbon dioxide through a bulb contained in a calorimeter, and obtained 39,300 cal. The procedure adopted by Raabe introduced a number of sources of error, however, one of which was pointed out by Matignon,² namely, that some of the carbamate formed might be carried away by the exit gases and thus lead to too high a result. Moreover, the quantity of carbamate used was small (0.3–0.8 g.), the observed temperature rise, therefore, being too small for the greatest accuracy.

Matignon² determined the heat of solution of ammonium carbamate and the heat of neutralization of dissolved carbamate with hydrochloric acid, deducing the heat of formation of ammonium carbamate from ammonia and carbon dioxide as 39,000 cal., at constant pressure. The data required in addition to those determined by Matignon, as well as their source, were not disclosed.

The direct method possesses advantages over other means, provided such sources of error as loss or insufficiency of material can be eliminated. In the direct method as adopted in the present study, loss of material was avoided by use of a closed system; the amount of carbamate formed was approximately 5 g., the temperature rise being sufficient to minimize observational error.

Apparatus and Procedure

The principal parts of the apparatus are shown in Fig. 1. A fully charged carbon dioxide cylinder A was connected to Cylinder B so that the latter could be brought to about 41 atmospheres' (610 lbs.) gage-pressure at the beginning of each experiment. Analysis showed the presence of less than

⁴ Lecher, *Sitzb. kgl. preuss. Akad. Wiss.*, II, Abth. October, 1878.

0.03% of moisture in the carbon dioxide. Further drying of the gas was not resorted to, since some moisture is required to enable the reaction to proceed; moreover, the possible influence of the amount found above could not be greater than 100 cal. per mole of carbamate. Twelve and two-tenths meters of small copper pressure tubing led from Cylinder B to Valve F, being immersed in the form of a coil D in the constant-temperature bath C. The tubing H from Valve F to the water level in the calorimeter was insulated to minimize radiation losses at this point. The bomb I of 415cc. capacity was fitted with a valve G which could be opened or closed by means of a small key inserted through a hole in the calorimeter cover.

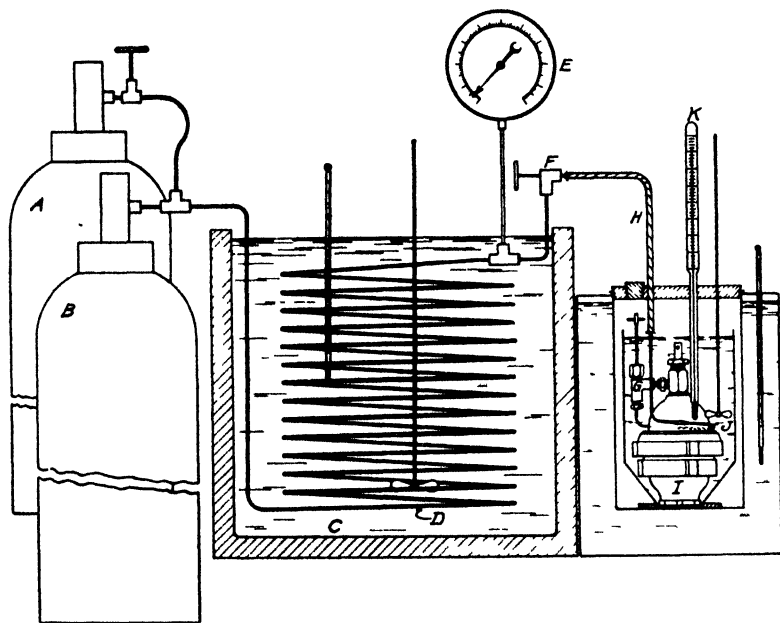


Fig. 1.

At the beginning of an experiment, the bomb was evacuated to a pressure of approximately 5 mm. of mercury, and anhydrous synthetic ammonia was admitted to a pressure of approximately 6.8 atmospheres absolute, which is about 1.7 atmospheres below saturation pressure at 21° . Higher pressures of ammonia were intentionally avoided to eliminate possible error through condensation of ammonia, and its subsequent vaporization during the determination. The bomb was then immersed in the calorimeter and connected to the carbon dioxide supply line at Valve F. The temperature of the room, the bath C, the calorimeter and the jacket having been brought to $21^{\circ} \pm 0.1^{\circ}$, the stirring rise over a preliminary period of six minutes was observed. At the end of this time, carbon di-

oxide was admitted by opening successively Valves F and G. To insure that the heat effect of expansion of the carbon dioxide would be reproducible in all experiments and measured in the calorimeter, the capillary tube J had been introduced as an orifice. The pressure attained equilibrium at approximately 40 atmospheres in about two minutes, Valves F and G being closed one minute later. Temperature readings were taken at 15-second intervals during the transfer period of about six minutes, after which the final cooling rate was determined. The amount of carbamate formed was determined by analysis, it being assumed on the basis of the relatively low vapor pressure of carbamate at 21° that the ammonia was completely combined in the presence of the large excess pressure of

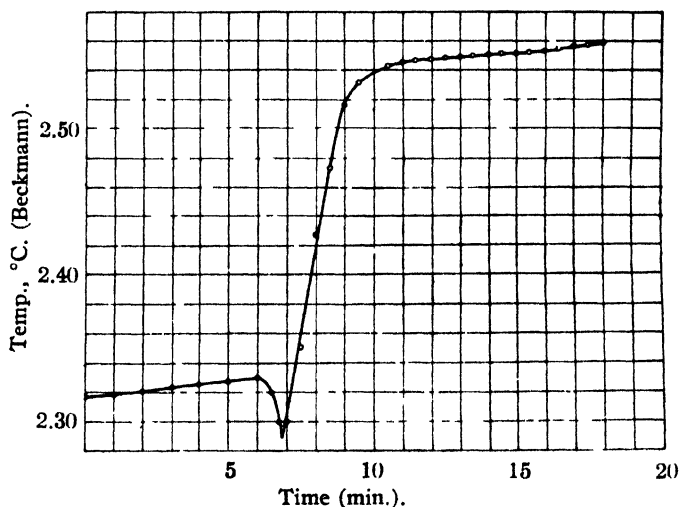


Fig. 2.—Carbon dioxide compression experiment. Initial pressure, 0.005 atmospheres (air); final pressure, 42.496 atmospheres (carbon dioxide), heat evolved, 427.0 cal

carbon dioxide employed for this purpose. The carbamate was collected under such conditions that the possibility of loss was entirely precluded, the excess of carbon dioxide being discharged and the bomb evacuated through standard acid. Water was then admitted to the bomb to dissolve the carbamate, and the solution withdrawn under vacuum with the standard acid trap in series. After several washings had been carried out in this manner to insure complete recovery, the solution of carbamate was made up to volume and analyzed for ammonia, the standard acid being back-titrated.

The "water equivalent" of the complete calorimeter assembly containing 1600 g. of water was determined in a preliminary series of experiments, in which a measured amount of heat was introduced electrically. The d. c. ammeter and voltmeter used were checked against instruments

of known accuracy, and during the heating period of five minutes these instruments were read at five-second intervals. The values obtained in four experiments ranged from 2071 to 2078 g. of water, or an average of 2075.

In a second series of preliminary experiments, the heat effect of the introduction of the carbon dioxide into the calorimeter bomb was measured in the absence of ammonia. For this purpose, the bomb was evacuated, immersed in the calorimeter and carbon dioxide was admitted to a pressure of 40 atmospheres' gage, the technique being identical with that to be used in later experiments with ammonia present. It was realized that in the

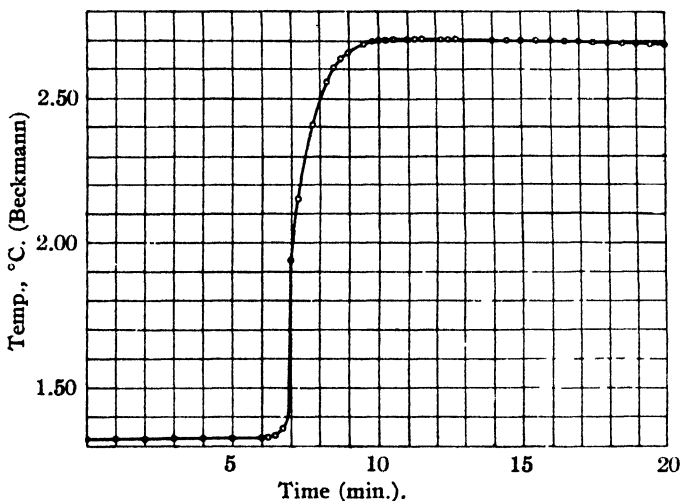


Fig. 3.—Expt. 14. Heat of reaction, $2\text{NH}_3 + \text{CO}_2 \longrightarrow (\text{NH}_3)_2\text{CO}_2$; initial pressure, 7.122 atmospheres (ammonia); final pressure, 42.633 atmospheres (carbon dioxide).

later experiments with ammonia present, the total amount of carbon dioxide entering the bomb would include the additional quantity required to react with the ammonia. This correction was subsequently calculated, for it could not be determined directly. The temperature rise observed in three experiments⁶ was 0.202, 0.204 and 0.207°, or an average of 0.205°, corresponding to the liberation of 427 cal. Fig. 2, which typifies these experiments, clearly shows the initial temperature drop due to the Joule-Thomson effect taking place within the calorimeter. It is interesting to note that the above value of 427 cal. is in good agreement with that obtained from theoretical considerations, which was 448 cal. This latter value was arrived at by calculating the Joule-Thomson effect at the orifice and the heat of compression in the bomb.

⁶ For convenience, these experiments will be referred to as carbon dioxide blanks.

Experimental Data and Method of Calculation

Table II and Fig. 3 present the time, temperature and other observations taken during a determination of the heat of reaction (Expt. 14). This material will be used to illustrate the procedure followed in the final calculations.

TABLE II
HEAT OF REACTION DATA (EXPT. 14)

Time, Min. sec.	Observed temp., °B. ^a	Time Min. sec.	Observed temp., °B.	Time, Min. sec.	Observed temp., °B.	Time Min. sec.	Observed temp., °B.
0	1.323	8	2.495	11 30	2.705	15	2.699
1 0	1.324	15	2.558	45	2.705	30	2.698
2 0	1.325	30	2.604	12	2.705	16	2.697
3 0	1.326	45	2.636	15	2.705	30	2.696
4 0	1.327	9	2.659	30 ^c	2.704	17	2.694
5 0	1.328	15 ^b	...	45	2.704	30	2.693
6 0	1.330	30	2.685	13	2.703	18	2.691
15 ^a	...	45	2.694	15	2.703	30	2.690
30	1.37	10	2.697	30	2.702	19	2.690
45	1.64	15	2.700	45	2.701	30	2.688
7	1.94	30	2.704	14	2.700	20	2.687
15	2.15	45	2.704	15	2.700		
30	2.30	11	2.704	30	2.699		
45	2.41	15	2.704	45	2.699		

^a Valve opened (beginning of transfer period).

^b Valve closed.

^c End of transfer period.

^d Beckmann thermometer readings.

The heat evolved by the formation of the carbamate may be expressed by the following equation, which takes into account the necessary corrections.

Heat evolved = $(A + B)(x + y + z) - C(x + y) - D = (1.345 + 0.0025)(2075 + 8.24 + 2.42) - 0.205(2075 + 8.24) + 26.3 = 2409.6$ cal., where A is the temperature rise of the transfer period after correction of the Beckmann readings for deviation of the latter from a Bureau of Standards compared thermometer;

$$B \text{ is the Regnault-Pfaundler cooling correction} = T_{tr} \left[V_p + \frac{V_c - V_p}{\theta_c - \theta_p} (\theta_{tr} - \theta_p) \right] = 6.25 \left[-0.00117 + \frac{0.00217 + 0.00117}{2.694 - 1.326} (2.380 - 1.326) \right] + 0.0025^\circ$$

T_{tr} is the time of the transfer period in minutes;

V_p , the cooling rate of preliminary period;

V_c , the cooling rate of final period;

θ_c , the mean temperature of final period;

θ_p , the mean temperature of preliminary period;

θ_{tr} , the mean temperature of transfer period;

C is the temperature rise (corrected as for A) of the transfer period in the carbon dioxide blank;

D , the Joule-Thomson effect in calories of that part of the carbon dioxide which enters into the reaction to form carbamate = $\Delta T N_1 C_{P_{CO_2}} = \mu N_1 C_{P_{CO_2}} (P - P_0) = (-1.15)(0.0665)(8.79)(42.8 - 3.7) = -26.3$ cal.;

T is the change in temperature in $^{\circ}\text{C}.$ of the carbon dioxide expanding through orifice J from mean effective pressure P of the carbon dioxide, at the source, against the mean pressure (P_0) of the ammonia in calorimeter bomb $= \mu(P - P_0) = -45^{\circ}$;

μ = Joule-Thomson coefficient for carbon dioxide $= -1.15^{\circ}$ per atmosphere;

N_1 = number of moles of entrant carbon dioxide combining to form carbamate;

$CP_{\text{CO}_2} = 7.0 + 0.0071 T + 0.00000186 T^2 = 8.79 \text{ cal.} = \text{molal heat capacity of carbon dioxide at mean of calorimeter and entrant gas temperatures;}$

x = heat capacity of the calorimeter assembly as determined $= 2075 \text{ g. cal. per deg.};$

y = heat capacity of the carbon dioxide in bomb (in excess of that required for the reaction) $= N_2 CP_{\text{CO}_2} = (0.922)(8.93) = 8.24 \text{ g. cal./deg.};$

N_2 = number of moles of carbon dioxide in excess of that required for the reaction (from van der Waals' equation of state);

C_P = molal heat capacity of carbon dioxide at 22° .

z = heat capacity of the carbamate formed $= N_3 CP_{(\text{NH}_4)_2\text{CO}_2} = 0.0665 (36.4) = 2.42 \text{ g. cal./deg.};$

N_3 = number of moles of carbamate formed $= 0.0665$;

$CP_{(\text{NH}_4)_2\text{CO}_2}$ = molal heat capacity of carbamate calculated from the molal heat capacities of the elements using the values $\text{C} = 1.8$, $\text{H} = 2.3$, $\text{O} = 4.0$, $\text{N} = 6.4$, assigned by Kopp⁶ $= 36.4 \text{ g. cal./mol./deg.}$

The 2409.6 cal. found as above is referred to the quantity of carbamate found by analysis, which in this case was 1.8624 g. of nitrogen, equivalent to 5.1892 g. or 0.0665 mole of carbamate; from which we obtain $\Delta U_p = 2409.6/0.0665 = 36,250 \text{ cal.}$ Five determinations gave the following results: 36,340, 36,350, 36,100, 36,250 and 36,480 cal., or an average of 36,300 cal.

The heat of reaction at constant pressure may be calculated from the above-determined value by the usual equation $\Delta U_p = \Delta U_v - \Delta nRT$, where Δn is the difference between the final and initial number of gas moles involved. The value thus obtained is 38,060 cal.

Summary

The heat of formation of ammonium carbamate from ammonia and carbon dioxide has been determined as 36,300 cal. per mole of carbamate at constant volume. This value, which was obtained by the direct method, is appreciably lower than previous experimental values, with the exception of Lecher's result of 37,700 cal. at constant pressure. It may also be noted that the value calculated from Naumann's vapor-pressure data in the range where accuracy of the latter might be expected (10 – 30°) is in good agreement with the results of the present study.

WASHINGTON, D. C.

⁶ Kopp, *Ann. Chem. Pharm. Supp.*, [1] 3, 289 (1864).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, No. 39]

THIOGLYCOLIC ACID AS A COLOR TEST FOR IRON

BY EDWARD LYONS

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The standard method for the identification of ferric iron is the thiocyanate method. The test is based on the red color formed when an alkali thiocyanate reacts with ferric iron in acid solution. This method, with various modifications, is used for the determination of small amounts of iron.

For the detection of ferrous iron in minute quantities, the dark blue ferrous ferricyanide test is used. This serves to indicate the presence of ferrous iron in ferric solutions.

The test under consideration in this paper is the color produced when the reaction mixture between thioglycolic acid and iron in solution is made faintly alkaline. The color so produced has long been known. Andreasch¹ described it in detail and Claësson² claimed that he was quite aware of the reaction. The interpretation of the reaction, however, we believe to be entirely different from what they claim. They believed that the color produced was due to the formation of the complex ferric thioglycolate, $\text{Fe}(\text{SCH}_2\text{COONH}_4)_3$. They further observed that the color faded after some time but was regenerated on shaking the solution with air. The fading of the color, they thought, was due to oxidation of part of the acid which then gave a colorless ferro salt. This in turn took up oxygen and gave the colored ferri salt. We differ entirely with the explanation of the mechanism of the color reaction as given by the above-mentioned investigators. The test has been found to be general for both ferric and ferrous iron. The red or purple color produced, however, is due to the reaction between ferrous iron and thioglycolic acid. In alkaline solution the color produced is pink in dilute solutions and intensely red-dish-purple in the more concentrated solutions. The test is applicable quantitatively in dilutions approximating one part of iron in about five million. Qualitatively, iron can be detected even in dilutions of 1:10 or 12 million. With thiocyanate the quantitative estimation of ferric iron in dilutions greater than several parts of iron per million presents considerable difficulty in color matching.

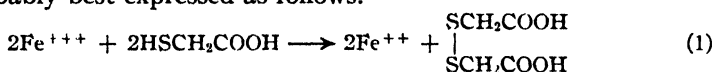
When ferric iron in concentration greater than 1:100,000 is present, the addition of thioglycolic acid yields a transient blue coloration. When the concentration is less, only a flash of blue may be observed. This is due to the formation of ferric thioglycolate, $\text{Fe}(\text{SCH}_2\text{COOH})_3$. However, this is at once reduced to the colorless ferrous thioglycolate, Fe -

¹ Andreasch, *Ber.*, 12, 1391 (1879).

² Claësson, *Ber.*, 14, 411 (1881).

$(\text{SCH}_2\text{COOH})_2$, complex, which yields the intensely colored ferrothioglycolate ion, $\text{Fe}(\text{SCH}_2\text{COO})_2^{--}$, in alkaline solution. If thioglycolic acid is similarly added to a solution of ferrous iron the blue coloration does not appear at all, but an intense red color is formed on making it alkaline. The presence of an oxidizing substance prevents the formation of the color. This is probably due to the formation of dithioglycolic acid, which does not yield color with either ferrous or ferric iron; its formation is the cause of the color fading observed by the previous investigators. The color cannot be regenerated by "shaking with air" nor by passing oxygen gas through the solution. On the contrary, fading of color results and when all of the thioglycolic acid has been oxidized the color can be brought back only by addition of more thio acid, or by means of a reducing agent which regenerates the thio acid in solution. Using ferric iron in the test and discharging the color formed with concd. hydrochloric acid, we no longer obtain a test for iron with thiocyanate, thus showing that the iron has been reduced to the ferrous condition. The addition of a drop of peroxide also discharges the color. It oxidizes not only the thio acid, but in the resulting solution thiocyanate gives a test for ferric iron.

The mechanism of the reaction between ionic iron and thioglycolic acid is probably best expressed as follows.



Reaction 1 occurs only when Fe^{+++} is present. As soon as it is reduced, Reaction 2 takes place, yielding the colored ion when an alkali is added. However, if an excess of acid or alkali is added the color is discharged. Neutralization of the excess reagent added again brings out the color.

Although the reaction is between ferrous iron and thioglycolic acid, both ferric and ferrous iron may be detected and estimated in the same solution. The color with thiocyanate due to ferric iron, which is stable in acid solution, is readily discharged by alkalis, while that produced by thioglycolic acid is stable in weakly alkaline solutions. Strong bases have to be used with considerable care, since a small excess discharges the color. Ammonia, however, does not appear to affect the intensity of the shade quickly, even when present in great excess. In time, however, a too great amount will show its effect. Since thioglycolic acid reduces ferric to the ferrous form, the total iron present can be readily estimated. The ferric iron can be determined with thiocyanate and the ferrous iron is then obtained by difference.

Qualitative Test.—To about 5 cc. of the suspected neutral or slightly acid solution free from oxidizing agents (these oxidize the thio acid), add one drop of thioglycolic acid and about 0.5 cc. of concd. aqueous ammonia.

If no color appears in about five minutes, no ionic iron is present in concentration greater than 1 to 10 or 12 million. When iron is present in concentration of 1 to 4 or 5 million or greater, the color appears at once. If it is of interest to know whether any ferric iron is present, a test with thiocyanate can be made first; then a drop of thioglycolic acid is added, and on addition of aqueous ammonia, in excess, the color due to ferric iron (if present) fades and the purple or pink color due to the ferrous-thioglycolic acid reaction appears. When the ammonia is added before the thio acid the maximum intensity of color appears somewhat more slowly.

The intensity of the color obtained with different concentrations of iron solutions led us to believe that the method would be applicable quantitatively. Accordingly, a series of solutions was made containing one part of iron in 100,000, 200,000, 300,000, etc., up to 12 millions. These were then used as unknowns. It was found that the difference between every two dilutions could be very easily detected and the particular concentration dealt with absolutely determined by comparison with known standards of similar solutions up to about 1 in 4 or 5 million parts. In greater dilutions the results were only qualitative. From these results we were able to develop a method for the determination of ferrous and ferric iron in any solution.

Quantitative Estimation of Total Iron (Ferric plus Ferrous)

(a) **Total Iron.**—The unknown solution is first tested qualitatively. From the intensity of the color obtained, a little experience soon teaches the experimenter to approximate the correct concentration. The dilution is then adjusted to about 1:500,000. When the solution is already very dilute the determination is made on the original, if feasible, or the solution is concentrated by evaporation. In the present work the color produced at about 1:500,000 was used. At this dilution the colors obtained are very easy to match, and the difference in intensity between, say 475,000 and 500,000, is distinct enough to allow an approximation of the intermediate dilutions very nicely. The solution prepared for testing is then transferred to a test-tube marked at 5cc. volume. To this is now added one drop of thioglycolic acid and 0.5 cc. of concd. aqueous ammonia. The color produced is then compared with the colors of standards of known concentration of iron. We then have: $\% \text{ Fe in unknown} = 100 \times \frac{\text{dilution of unknown}}{\text{dilution of standard}} \div \text{amount used (g. or cc.)}$; multiplying by 10,000 we have parts per million; that is, if 1.0 cc. of an unknown is diluted to a final volume of, say, 5000 and compared with a 1:400,000 standard, then $\% \text{ Fe in unknown} = 100 \times (5000/400,000) \div 1 = 1.25$, or 12,500 parts per million.

Likewise, if 0.2 g. of substance is dissolved to give a solution containing one part in 10,000, and the color of this agrees with that of a 1:300,000 standard, then $\% \text{ Fe} = 100 \times (10,000/300,000) \div 0.2 = 0.067$.

(b) **Ferric Iron.**—By using potassium thiocyanate in a hydrochloric acid solution of the unknown and comparing with colors of standard solutions, the ferric iron may be estimated as usual. If the sample at hand is not of sufficient quantity to permit a separate determination, then both ferric and ferrous iron may be determined in the one sample before the estimation of the "total iron." A drop or two is tested with potassium thiocyanate. If ferric iron is indicated, a quantitative estimation on the major part of the sample is made. This gives us the ferric iron. To this solution is now added a few drops of aqueous ammonia, to discharge the color due to ferric iron, the ammonium hydroxide is neutralized with hydrochloric acid, since it delays the appearance of the color, then one drop of thioglycolic acid is added. Ammonium hydroxide now added in slight excess gives the color due to the total iron reduced to the ferrous condition.

(c) **Ferrous Iron.**—From the total iron (estimated as ferrous) subtract the ferric iron (potassium thiocyanate method). The difference is the ferrous iron originally present.

TABLE I
DETERMINATION OF IRON IN SOME SAMPLES

Substance	Iron found	Iron by analytical method, or calcd.	Remarks
Sol. Fe Chloride	10.0%	10.2%	
Colloidal Fe Soln.	0.0114 g. per cc.	0.0119 g. per cc.	Decomp. with HCl
$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	14.02%	14.25%	
U. S. P. Iron Quinine Citrate	12.5%	$13.00 \pm \%$	
Iron Cacodylate	0.00155 g. per cc.	0.00160 g. per cc.	

TABLE II
ANALYSIS OF MIXTURES OF FERROUS AND FERRIC IRON

Mixtures containing known amounts of ferric and ferrous iron were made. Ferric iron was determined by the potassium thiocyanate method. Total iron was obtained by the thioglycolic acid method. The difference gave the ferrous iron.

Ferric iron, g.		Total iron, g.		Ferrous iron, g.	
Taken	Found	Taken	Found	Taken	Found by diff.
0.0001	0.0001	0.00015	0.00016	0.00005	0.00006
.00018	.0002	.00026	.0003	.00008	.00010
.00004	.000036	.00018	.00018	.00014	.000144

The following substances (0.01 g. per cc. of 1:500,000 ferric solution) did not appear to affect the delicacy of the reaction.

Sodium acetate, arsenate, bromide, benzoate, citrate, cacodylate, chloride, fluoride, glycerophosphate, iodide, phosphate, pyrophosphate, salicylate (use three or four drops of thio acid), sulfate, sulfite, sulfocarbolate, thiosulfate, etc.

Also salts of the following metals: potassium, lithium, barium, calcium, strontium, and, if not in too large amounts, mercury, copper, cadmium, zinc, tin, magnesium, silver, bismuth, etc. When these are present in the order of the concentration of the iron no interference is observed (especially when three or four drops of thio acid are used). Large amounts (0.001 g. per cc. or more) which of themselves give a color with the acid or tend to precipitate with aqueous ammonia may affect the delicacy of the test. The addition of some sodium citrate will in such cases often bring out the full color due to the iron present.

Summary

Thioglycolic acid is recommended as a delicate color test for iron. This reagent³ is capable of detecting iron in dilutions up to 1:10,000,000 and is relatively much more delicate than the usual thiocyanate test. Moreover, the test is independent of the state of oxidation of the iron since it is given equally well with either ferrous or ferric iron in contrast with the thiocyanate test which is sensitive only to ferric iron.

A study of the reaction of thioglycolic acid with iron has shown that the reagent is really a test for ferrous iron, but since the reagent itself promptly reduces ferric iron to the ferrous state we have here a general test for ionic iron.

Since the thioglycolic acid test is applied in ammoniacal solution, a condition under which the color obtained with ferric iron and thiocyanate is completely discharged, the two tests may be applied to the same solution in succession.

The thioglycolic acid test is capable of quantitative application. Used in conjunction with the thiocyanate test we have here a simple method of estimating both ferric and ferrous iron in the same solution by colorimetric methods.

DETROIT, MICHIGAN

³ Thioglycolic acid is now being supplied by the Eastman Kodak Co.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

**DIFFUSION-POTENTIAL MEASUREMENTS APPLIED TO
HYDROCHLORIC ACID-GELATIN SYSTEMS. I. THE
EQUIVALENT WEIGHT OF GELATIN¹**

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In this article an apparatus is described which permits the approximate measurement of a static liquid-junction potential between hydrochloric acid of two concentrations and of more complex systems of hydrochloric acid-sodium chloride. The measurements are also extended to systems of hydrochloric acid-gelatin. The striking similarity between these systems and those of hydrochloric acid-sodium chloride favors the establishment of gelatin-acid solutions as true solutions. The stoichiometric character of the combination between gelatin and acid is demonstrated and the equivalent weight of gelatin determined.

If two different electrolytic solutions are placed in contact, there is developed at the junction a potential difference which is called a diffusion potential. This potential is caused by the unequal migration velocities of the ions in the two solutions, that is, in simple electrolytes or mixtures of electrolytes the potentials are determined by the ionic activities and the ionic mobilities.

In a boundary such as



the potential is zero since identical solutions are on each side of the contact layer. If, however, sodium hydroxide replaces part of the hydrochloric acid in one of the solutions in such a manner that the mixture always has a constant concentration of 0.10 *N*, a potential develops which becomes increasingly greater as the solution ultimately approaches 0.10 *N* sodium chloride, since the hydrogen ion is being replaced by the slower-moving sodium ion.

If in an identical arrangement as the above gelatin is substituted for the sodium hydroxide, the resulting potentials should give some information as to the physical state of the resulting mixtures, that is, whether as Loeb and others have maintained, gelatin reacts stoichiometrically with hydrochloric acid, forming highly ionized gelatin chloride,² or whether an adsorption complex of some sort is formed,³ or whether the type of

¹ The material presented in this article is constructed from a portion of the thesis submitted to the Graduate School of the University of Michigan by Egbert K. Bacon in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² (a) Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Co., New York, 1922. (b) Hitchcock, *J. Gen. Physiol.*, **5**, 383 (1923). (c) Procter, *J. Chem. Soc.*, 105, 313 (1914).

³ (a) Shukov and Shchukarev, *J. Phys. Chem.*, **29**, 285 (1925). (b) Alexander, "Glue and Gelatin," Chemical Catalog Co., New York, 1923. (c) de Izaguirre, *Kolloid-Z.*, **32**, 47 (1923). (d) Bracewell, *THIS JOURNAL*, **41**, 1511 (1919).

combination might be due partly to purely chemical forces and partly to forces of adsorption, as Hoffman and Gortner suggest.⁴

In order to carry out such measurements it was necessary to devise an apparatus that would permit the measurement of such potentials between solutions of high viscosity. Its reliability was first demonstrated with simpler electrolytic solutions.

Hydrochloric Acid Cells

The apparatus used in the investigation is illustrated by Fig. 1. A and B are two glass vessels filled with solutions M and M'. CGD is a three-way stopcock of 9 mm. bore. The two siphon arms are indicated.

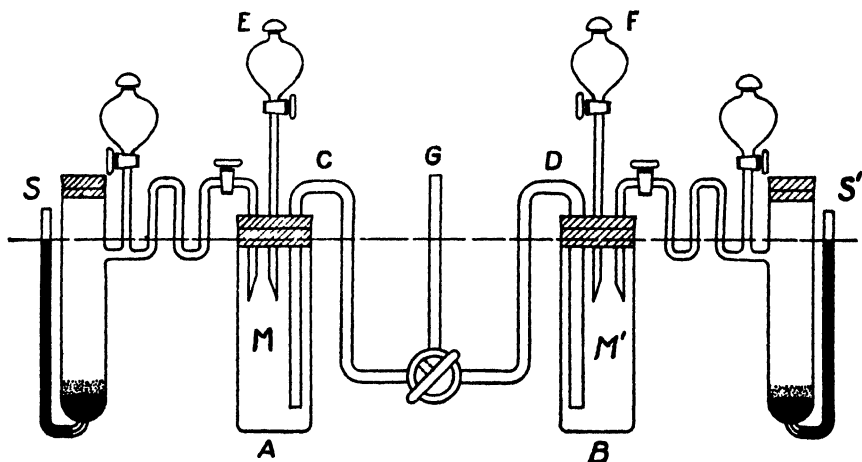
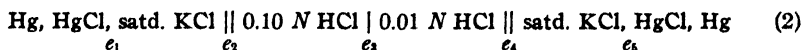


Fig. 1.—Apparatus with saturated potassium chloride electrodes for the measurement of diffusion potentials.

E and F are dropping funnels and S and S' saturated potassium chloride electrodes. The liquid junction was made in the stopcock between the two siphon arms by proper manipulation of the stopcock and the application of suction through G.

Potential measurements were first made with a simple boundary which is illustrated by the following cell,



Such a cell is made up of five potentials e_1 , e_2 , e_3 , e_4 and e_5 . Potentials e_1 and e_5 are equal and oppositely directed, and the same is considered

⁴ Hoffman and Gortner, "Colloid Symposium Monograph II," Chemical Catalog Co., New York, 1925, p. 209. This work has been criticized by Cohn, *Physiol. Rev.*, 5, 349 (1925).

approximately true for e_2 and e_4 .⁵ Hence, the measured total potential of such a cell must be due almost entirely to the diffusion potential e_3 .

The potential measurements were made by means of a Queen Gray Standard type potentiometer which gave readings to 0.01 mv. The standard cell was a Weston cadmium cell which was checked against another cell certified by the Bureau of Standards. All measurements were carried out in an oil thermostat at 25° regulated to $\pm 0.015^\circ$. Observations were made by means of a telescope placed 12 feet from a Leeds and Northrup galvanometer No. 2500E with a sensitivity of 362 megohms.

The calomel-electrode vessels were of the Lewis type.⁶ The usual precautions were taken in making up the saturated potassium chloride electrodes and only the purest of chemicals used. The electrodes were checked with each other frequently and usually showed potentials below 0.10 mv. If at any time two reference electrodes showed potentials greater than 0.20 mv. they were discarded.

The hydrochloric acid solutions were made by dilution of a stock solution of 1 *N* hydrochloric acid which in turn was made from a standard, analyzed hydrochloric acid solution.

The concentration cells were made up and left in the bath for at least one hour before measurements were taken. When a cell had attained the temperature of the bath the stopcock was opened, the liquid junction established and a reading taken immediately. The stopcock was then closed. Another reading was taken shortly afterward. In all cases readings were taken with stopcock open; then the stopcock was immediately closed. Readings were taken in this manner at approximately hour intervals, until the potential of the cell started to drop rapidly. This usually resulted after a period of 40 hours.

The results obtained were very satisfactory. Three cells gave average values of 38.08, 38.08 and 38.11 mv. over a period of about 35 hours. These values represent the averages of about 20 readings taken over this period. The "time effects" were not large, amounting to less than 0.5 mv. It may be concluded, therefore, that the apparatus is capable of giving constant and reproducible potentials with this simple type of boundary.⁷

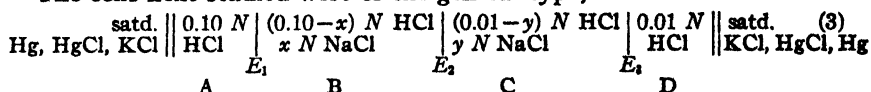
⁵ Loomis and Acree [*Am. Chem. J.*, **46**, 585 (1911)], Fales and Vosburgh [*THE JOURNAL*, **40**, 1291 (1918)] and others have shown that the diffusion potential between saturated potassium chloride and solutions of hydrochloric acid and sodium chloride below 0.1 *N* is zero or at any rate very small, that is, the order of a few tenths of a millivolt. More recently, Scatchard [*ibid.*, **47**, 696 (1925)] claims that the potential between saturated potassium chloride and concentrations of hydrochloric acid below 0.1 *N* is constant and has the value of 4.7 mv.

⁶ Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

⁷ Calculated values of this boundary, by the Nernst equation indicate that the potential closely approximates 38 mv.

Hydrochloric Acid-Sodium Chloride Cells

The cells next studied were of the general type,



The cells were made up of four solutions A, B, C and D. A represents 0.10 *N* hydrochloric acid, the same in all of the cells; B represents a mixture of hydrochloric acid and sodium chloride of total concentration 0.10 *N*, in which *x* varies in different cells from 0 to 0.10; C represents a mixture of hydrochloric acid and sodium chloride of total concentration 0.01 *N*, in which *y* is equal to *x* until the value 0.01 is reached and then remains constant while *x* in the other solution changes until it reaches its final value of 0.10; D represents a solution of 0.01 *N* hydrochloric acid, the same in all cells.

The sodium chloride solutions in the mixtures were formed by partial neutralization of the hydrochloric acid. The sodium hydroxide used for this purpose was made by dilution of the solution formed by the electrolysis of sodium amalgam. Its concentration was determined by titration with hydrochloric acid.

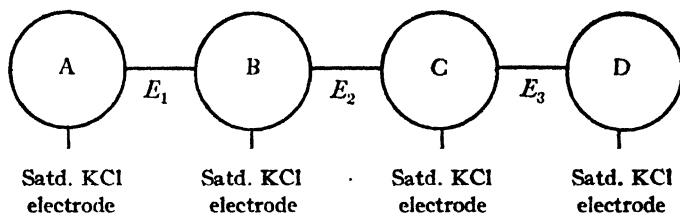


Fig. 2.—Arrangement of cell for diffusion potential measurements.

The total potential of the above cell is made up of three different diffusion potentials E_1 , E_2 and E_3 at the solution contacts A-B, B-C and C-D. The cell shown in Fig. 1 permits the measurement of a single diffusion potential. By means of three such cells joined together, and with the use of four saturated potassium chloride electrodes, it is possible to measure each of the three boundary potentials E_1 , E_2 and E_3 individually, or combinations of the three. The arrangement of the cell is illustrated by Fig. 2.²

The method of setting up the cells and the manner of taking the readings were exactly as described for the hydrochloric acid cells. After the cell had attained the temperature of the bath, readings were taken at hour intervals for a period of about 12 hours.

Table I serves as a typical example of the results obtained with Bound-

² It is apparent that each diffusion potential involves the measurement of perhaps three boundaries, but the two boundaries $\text{satd. KCl} \mid \text{solution}$ and $\text{solution} \mid \text{satd. KCl}$, as noted before, probably have but little influence on the principal potential; hence, the diffusion potential is closely approximated in each case.

ary E_1 . This is characteristic of the results with Boundaries E_2 and E_3 . In the table the type cell is indicated at the top and the arrow from left to right indicates the direction of positive current through the cell. Duplicate cells were measured for each boundary and these are labeled Cell A and Cell B. The first entry under "Time" gives the hour at which the cell was first placed in the bath.

TABLE I
MEASUREMENTS WITH BOUNDARY E_1
Type Cell

Hg, HgCl, satd. KCl 0.10 <i>N</i> HCl $\left\{ \begin{array}{l} 0.08N \text{ NaCl} \\ 0.02N \text{ HCl} \end{array} \right\}$ satd. KCl, HgCl, Hg									
<i>E</i> ₁									
Cell A					Cell B				
Time		Potential, mv.			Time		Potential, mv.		
9:30	A. M.				9:45	A. M.			
11	A. M.	20.70			11	A. M.	21.11		
12	M.	21.02			12	M.	21.37		
1	P. M.	21.10			1	P. M.	21.34		
2	P. M.	21.06			2	P. M.	21.17		
3	P. M.	21.09			3	P. M.	21.03		
4	P. M.	21.00			4	P. M.	21.07		
5	P. M.	20.95			5	P. M.	20.88		
6	P. M.	21.03			7	P. M.	20.97		
7	P. M.	21.00			8	P. M.	20.90		
8	P. M.	21.06							
10	P. M.	21.02							
		Av.	+21.00				Av.	+21.08	

A summary of the measured values obtained with the various cells and the different boundaries is given in Table II. Col. 1 indicates the particular boundary measured; Col. 2, the value for the initial reading with Cell A; and Col. 3 the average of all readings for Cell A. Cols. 4 and 5 give similar readings with Cell B. Col. 6 gives the average of values in Cols. 3 and 5, and Col. 7, the averages of Cols. 2 and 4. The figures in parentheses after the potential values in Cols. 3 and 5 indicate the number of readings with the corresponding period in hours which the average value represents. For instance, (11-12) means 11 readings over a period of 12 hours.

An examination of the tables shows that the diffusion potentials of these more complex boundaries are as accurately reproducible as those of simpler systems, and in most instances appreciable "time effects" are not noticeable.

Hydrochloric Acid-Gelatin Cells

The hydrochloric acid-gelatin cells were of the following type,

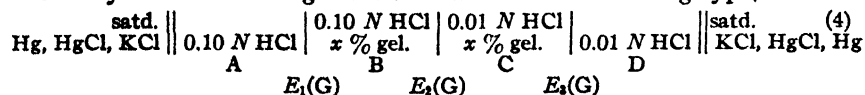


TABLE II
SUMMARY OF POTENTIALS FOR VARIOUS DIFFUSION BOUNDARIES

	Boundary		Initial E , Cell A, mv.	Average total E , Cell A, mv.	Initial E , Cell B, mv.	Average total E , Cell B, mv.	Average total E , Cells A and B, mv.	Average initial E , Cells A and B, mv.		
$2E_1$	0.10N HCl	0.004 NaCl	+ 0.79	+ 1.05	(11-12)	+ 1.27	+ 1.09	(13-13)	+ 1.07	+ 1.03
	0.10N HCl	0.096N HCl								
$3E_1$	0.10N HCl	0.01N NaCl	2.12	2.18	(11-12)	1.96	1.91	(7-8)	2.04	2.04
	0.10N HCl	0.09N HCl								
$4E_1$	0.10N HCl	0.04N NaCl	8.43	8.33	(12-12)	8.02	8.13	(10-12)	8.23	8.22
	0.10N HCl	0.06N HCl								
$5E_1$	0.10N HCl	0.08N NaCl	20.70	21.00	(11-12)	21.11	21.08	(9-10)	21.04	20.90
	0.10N HCl	0.02N HCl								
$6E_1$	0.10N HCl	0.10N NaCl	30.30	29.94	(12-12)	30.37	29.99	(9-12)	29.96	30.33
	0.10N HCl	0.01N HCl	38.52	38.08	(19-32)	38.57	38.08	(17-34)	38.08	38.54
$2E_2$	0.004N NaCl	0.004N NaCl								
	0.096N HCl	0.006N HCl	42.96	42.81	(11-12)	43.02	43.13	(11-12)	42.97	42.99
$3E_2$	0.01N NaCl									
	0.09N HCl	0.01N NaCl	55.71	55.54	(11-12)	56.14	56.09	(7-8)	55.81	55.92
$4E_2$	0.04N NaCl									
	0.06N HCl	0.01N NaCl	43.22	41.91	(12-12)	43.33	42.09	(11-12)	42.00	43.27
$5E_2$	0.08N NaCl									
	0.02N HCl	0.01N NaCl	15.32	12.81	(11-12)	14.79	13.01	(9-10)	12.09	15.05
$6E_2$	0.10N NaCl	0.01N NaCl	-10.70	-10.59	(12-12)	-10.51	-10.61	(9-11)	-10.60	-10.60
	0.004N NaCl									
$2E_3$	0.006N HCl	0.01N HCl	8.72	8.79	(11-12)	8.53	8.68	(11-12)	8.73	8.62
	0.01N NaCl	0.01N HCl	30.00	29.49	(12-11)	30.00	29.73	(11-11)	30.00	29.61

These cells were made up of four solutions, A, B, C and D. A represents a solution of 0.10 *N* hydrochloric acid, the same in all cells. B represents a solution of $x\%$ gelatin in 0.10 *N* hydrochloric acid, in which x is the number of grams of gelatin present in 100 cc. of solution, and varies from 0 to 17.4 in the different cells. C represents a solution of $x\%$ gelatin

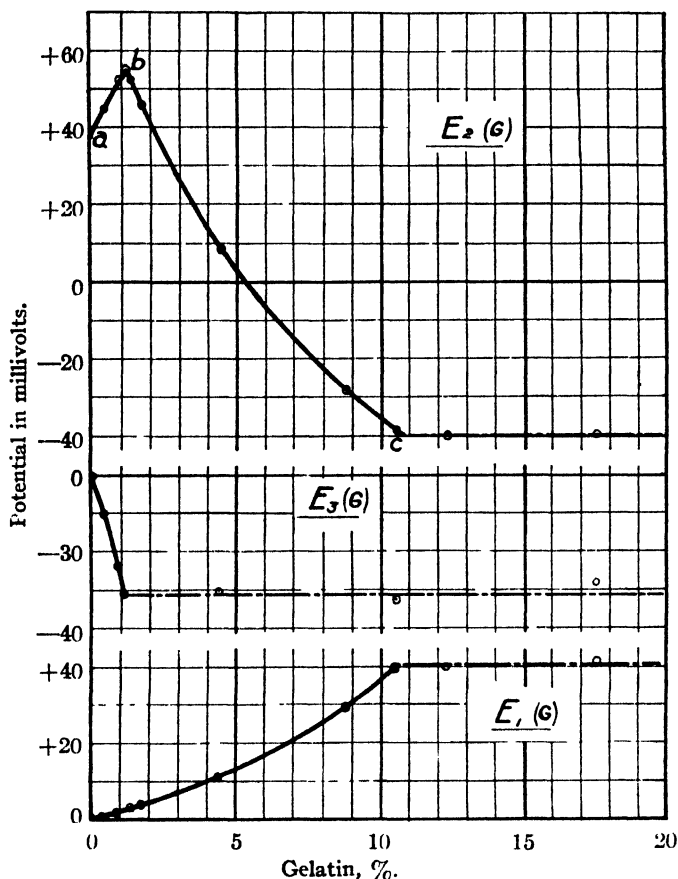


Fig. 3.—The diffusion potentials for boundaries $E_2(G)$, 0.10*N* HCl + $x\%$ gelatin | 0.01*N* HCl + $x\%$ gelatin; $E_3(G)$, 0.10*N* HCl + $x\%$ gelatin | 0.01*N* HCl; $E_1(G)$, 0.10*N* HCl | 0.10*N* HCl + $x\%$ gelatin.

in 0.01 *N* hydrochloric acid, where x again represents the number of grams of gelatin in 100 cc. of solution and varies between the limits 0 and 17.4 in the different cells. D represents a solution of 0.01 *N* hydrochloric acid, the same in all cells.

The total potential of this cell is made up of three diffusion potentials formed by the contacts of Solutions A and B, B and C, and C and D.

These are E_1 (G), E_2 (G) and E_3 (G) as indicated. Four saturated potassium chloride electrodes, one dipping in each solution, permit the measurement of any boundary or combination of boundaries.⁹

The hydrochloric acid solutions were made by dilution of an analyzed solution of 1 *N* hydrochloric acid, as described with the previous cells.

The gelatin was a pure ash-free (0.04% ash) iso-electric gelatin obtained from the Research Laboratories of the Eastman Kodak Company. The moisture content of the gelatin was about 12.6%. This was determined by heating 2 to 3g. samples in the drying oven at 110° until constant weight was obtained. The moisture content was applied as a correction to all weighings of gelatin.

A uniform procedure was used in preparing the gelatin solutions. The manner in which a 2% solution (which corresponds to a 1.75% solution when the moisture correction is applied) of gelatin in 0.10 *N* hydrochloric acid was prepared serves as an illustration of the general way in which all solutions were obtained.

Ten g. of gelatin (8.74 g. of the dry gelatin) was weighed to the nearest milligram. This was dissolved in distilled water at a temperature of about 35°. The solution of gelatin was then poured into a 500cc. flask and water added so that the volume was between 300 and 400 cc. A volume of 50 cc. of 1 *N* hydrochloric acid was then run in by means of a calibrated pipet and water was added to bring the volume to 500 cc. The solution of 2% gelatin in 0.01 *N* hydrochloric acid was made up in exactly the same way, 50 cc. of the 0.10 *N* hydrochloric acid being used instead of 1 *N* hydrochloric acid.

There was no difficulty encountered in making up these solutions, although with higher concentrations of gelatin they were very viscous and set to gels within a short time. The gel was easily melted by placing the flask in warm water. After this procedure it would not set to a gel until some time afterward, so that there was no trouble in filling the cells and making the boundaries.

The cells were filled and the boundaries made in exactly the same manner as previously described with the hydrochloric acid-sodium chloride cells. Readings were extended over a much longer period than with the other systems, usually over 24 hours. Since it seemed desirable to experiment with these cells under as rigorous conditions as possible, so that any consistent or reproducible results which might be obtained could not necessarily be ascribed to an empirical procedure, duplicate cells were measured under as varied conditions as possible, and in many instances entirely new gelatin solutions were made up. All measurements were carried out at 25°.

⁹ With considerations as noted before (see Ref. 5).

Results

The information given in Table III is typical of the results obtained with other cells. This table gives measurements with cells containing 0.874% of gelatin.

TABLE III
MEASUREMENTS ON CELLS WITH 0.874% OF GELATIN
Type Cell

Time	$\begin{array}{c} \text{satd.} \parallel 0.10 \text{ N} \parallel 0.10 \text{ N HCl} \parallel 0.01 \text{ N HCl} \parallel 0.01 \text{ N} \parallel \text{satd.} \\ \text{Hg, HgCl, KCl} \parallel \text{HCl} \parallel 0.874\% \text{ gel.} \parallel 0.874\% \text{ gel.} \parallel \text{HCl} \parallel \text{KCl, HgCl, Hg} \\ \xrightarrow{E_1(\text{G})} \quad \quad \quad \xrightarrow{E_2(\text{G})} \quad \quad \quad \xleftarrow{E_3(\text{G})} \\ \xrightarrow{\hspace{1.5cm}} \end{array}$					
	Cell A					
	$E_1(\text{G}), \text{mv.}$	$E_2(\text{G}), \text{mv.}$	$E_3(\text{G}), \text{mv.}$	$E(\text{G}), \text{mv.}$	$E_s(\text{G}), \text{mv.}$	
5:30 P. M.						
7 P. M.	1.95	52.32	24.57	29.30	29.70	
7:45 P. M.	1.87	52.32	23.57	30.70	30.62	
8:30 P. M.	2.19	52.45	23.05	30.86	31.59	
9:15 P. M.	1.86	52.31	23.03	31.03	31.14	
10:15 P. M.	1.85	52.30	23.06	31.13	31.09	
11:10 P. M.	1.87	52.34	23.06	31.16	31.15	
9:15 A. M.	2.20	52.01	23.72	30.13	30.49	
10:30 A. M.	1.95	52.10	23.72	30.41	30.33	
11:45 A. M.	2.03	52.26	23.55	30.62	30.74	
6:30 P. M.	1.86	52.35	23.48	30.76	30.73	
8 P. M.	1.88	52.30	23.55	30.53	30.63	
10 P. M.	2.14	52.03	23.45	30.58	30.72	
9:30 A. M.	1.86	52.04	23.24	30.59	30.74	
Av.	+1.96	+52.24	-23.46	+30.59	+30.74	
Cell B						
10:30 A. M.						
12 M.	1.95	52.11	25.28	28.75	28.98	
1:30 P. M.	2.07	52.02	24.83	29.26	29.26	
2:30 P. M.	1.88	52.28	23.65	30.22	30.51	
4 P. M.	1.93	52.25	23.84	30.41	30.34	
5:15 P. M.	2.08	52.23	24.33	30.02	29.48	
7 P. M.	1.90	52.45	23.97	30.32	30.41	
8 P. M.	1.84	52.52	24.01	30.35	30.44	
9 P. M.	1.82	52.28	24.05	30.28	30.05	
10 P. M.	2.08	52.17	24.22	30.04	30.03	
9 A. M.	1.77	52.05	23.82	29.82	30.00	
12:30 P. M.	1.88	52.11	23.75	29.86	30.04	
9:30 P. M.	1.85	51.97	23.72	29.93	30.10	
Av.	+1.90	+52.20	-24.11	+29.95	+29.97	

At the top of the table is indicated the type cell with the boundaries $E_1(\text{G})$, $E_2(\text{G})$ and $E_3(\text{G})$. Small arrows give the direction of flow of positive current in each boundary and a large arrow indicates the positive

or negative character of the entire cell; if from left to right the potential is considered to be positive and if from right to left negative. The first half of the table gives the measured values with Cell A and the second half those with Cell B. The first entry under "Time" gives the hour at which the cell was first placed in the thermostat bath. Successive entries give the time when measurements on the various boundaries were made. The readings in millivolts obtained with the three boundaries are given in the columns labeled $E_1(G)$, $E_2(G)$ and $E_3(G)$. In columns $E(G)$ and $E_s(G)$ are given the measured values for the total cell and also the values as determined from the algebraic sums of the boundaries.

It can be seen in both Cells A and B that in most instances the "time changes" in boundaries are very small, being of the order of a few tenths of a millivolt. The averages of the duplicate cells are very good.

Cells containing 0.437, 1.31, 1.75, 4.47, 8.74, 10.49, 12.23 and 17.48% of gelatin were treated in a manner similar to that illustrated in Table III.¹⁰

With higher concentrations of gelatin the "time changes" in boundaries $E_1(G)$ and $E_2(G)$ became more noticeable, although they consisted of fluctuations from hour to hour and did not show a general drift in any given direction. The 8.74% gelatin solutions became very viscous and overnight the gelatin in 0.01 *N* hydrochloric acid set to a gel. This had little effect on the boundary as comparison between readings taken at night and those taken the following morning showed only a change of 0.35 mv. and 0.20 mv. on two separate cells. With the 17.48% gelatin cells both gelatin solutions changed to gels within a few hours, but this change in state showed no noticeable effect on any of the potentials. In general, the agreement between duplicate cells and the deviations in readings in the single boundaries were not so good with the higher concentrations of gelatin, that is, above 10% of gelatin, but the potentials were perfectly definite. However, this irregularity at the higher concentrations introduced no difficulty since the significant conclusions are based upon results obtained at lower concentrations.

In practically every case values for duplicate cells agreed to less than 0.5 mv. and in most cases to within a few tenths of a millivolt. This shows that diffusion potentials with the supposedly complex gelatin systems are as accurately reproducible and as definite as with the simpler hydrochloric acid-sodium chloride systems.

In the cells containing more than 1.09% of gelatin, Boundary $E_3(G)$ showed a rather erratic behavior, the initial value for the boundary being much larger than any of the other values. This fall in potential amounted to as much as 10.7 mv. in ten hours. The reason for the apparent "time

¹⁰ The original thesis may be consulted for detailed measurements on these cells.

effect" in this boundary and others was made the subject of a special investigation and has been satisfactorily explained.

The graphical representation of the changes in diffusion potential in the different cells with the amount of gelatin added is given in Fig. 3, Curves $E_1(G)$, $E_2(G)$ and $E_3(G)$. In all instances the percentage of gelatin added to the solutions is plotted against the potential in millivolts.

Curve $E_1(G)$ shows the change in potential for Boundary $E_1(G)$ with increasing amounts of gelatin where x , the amount of gelatin in 100 cc. of solution, varies from 0.437 to 17.4 g. This potential starts at zero, since there is 0.10 *N* hydrochloric acid on each side of the boundary, increases gradually as gelatin is added to one side and finally reaches a maximum of +40 mv., when the gelatin concentration is about 10.9%. Beyond this concentration, as more gelatin is added, the potential remains practically constant in the region of +40 mv.

Curve $E_3(G)$ shows the changes in potential for Boundary $E_3(G)$. The potential starts at zero, since 0.01 *N* hydrochloric acid is on both sides of the boundary. As gelatin is added to one of these solutions, that is, as x varies from 0.437 to 17.4, the potential becomes increasingly more negative very rapidly, and soon reaches a limiting value of -31.50 mv. at 1.09% gelatin concentration. With higher concentrations of gelatin the potentials become largely indeterminate, although they tend to remain in the region of -31 mv.

Curve $E_2(G)$ represents Boundary $E_2(G)$, where x again varies from 0.437 to 17.4. The potential for this boundary starts with that between 0.10 *N* and 0.01 *N* hydrochloric acid, increases gradually as equal amounts of gelatin are added to both solutions and finally reaches a maximum of +54.97 mv. at a concentration of 1.09%. As more gelatin is added to both sides, that is, as x continues to increase, the potential drops rapidly, becomes negative and finally reaches a minimum of about -39 mv. It then remains constant for higher gelatin concentrations. The minimum point on the curve corresponds to a gelatin concentration of about 10.9%.

In Fig. 4 are given graphically the results with the hydrochloric acid-sodium chloride cells which have been previously described. The boundaries are indicated under each curve. The number of cc. of sodium hydroxide solution added to produce the hydrochloric acid-sodium chloride mixtures are plotted against the resulting potentials in millivolts.

Equivalent Weight of Gelatin from Diffusion-Potential Curves

If the curves for the hydrochloric acid-sodium chloride systems are compared with the curves for the hydrochloric acid-gelatin systems, it will be noted that their general appearance is strikingly similar. This would seem to indicate that the mechanism which is the cause of the

potentials in the hydrochloric acid-gelatin systems is perhaps similar to that of the hydrochloric acid-sodium chloride systems and interpretations that might be applied to the latter could also be applied to the former.

In the hydrochloric acid-sodium chloride curves, the maximum and minimum points on each curve correspond to the condition where complete

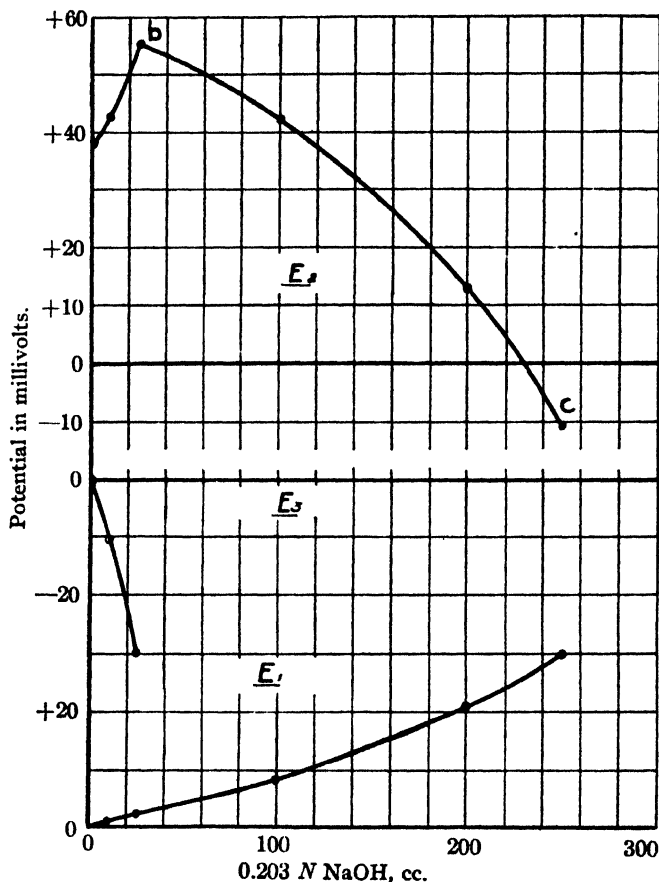


Fig. 4.—Diffusion potential changes with boundaries E_2 $(0.10 - x)$ N $HCl + x$ N $NaCl$ | $(0.1 - y)$ N $HCl + y$ N $NaCl$; E_3 $(0.01 - y)$ N $HCl + y$ N $NaCl$ | 0.010 N HCl ; E_1 0.10 N HCl | $(0.10 - x)$ N $HCl + x$ N $NaCl$.

combination between hydrochloric acid and sodium hydroxide has occurred. It seems clear from examination of the hydrochloric acid-gelatin curves that the four points of inflection on these three curves must indicate definite regions where complete combination between gelatin and hydrochloric acid has taken place. On both Curves $E_2(G)$ and $E_3(G)$ the first breaks occur at a gelatin concentration of 1.09%. This would correspond

to an equivalent weight of gelatin of 1090, since the solution at this point contains 1.09 g. of gelatin in 100 cc. of 0.10 *N* hydrochloric acid, and hence 1090 g. of gelatin would be necessary to combine with one equivalent weight of hydrochloric acid. On Curve $E_1(G)$ the first break and on Curve $E_2(G)$ the second break occur at a concentration of close to 10.9%, which corresponds to a condition where gelatin has combined with all the 0.10 *N* hydrochloric acid. This again gives the equivalent weight of gelatin as close to 1090.

These curves offer a striking proof that combination between gelatin and hydrochloric acid at concentrations ranging from 0.01 *N* to 0.10 *N* occurs in stoichiometric proportions, and the amount of gelatin which will combine with one equivalent weight of hydrochloric acid is 1090.

Other values which have been obtained for the equivalent weight of gelatin are given in a summarized form in Table IV. The results obtained in this work compare favorably with Hitchcock's values and also with those calculated by Greenberg and Schmidt.

TABLE IV
VALUES FOR THE EQUIVALENT WEIGHT OF GELATIN

Equiv. wt	Method	Equiv. wt.	Method
665	Electrometric titration ^a	1319-2083	Titration ^A
839	Titration ^b	1180	Titration ⁱ
1428	Titration ^c	1087	Electrometric titration ^j
1176	Calcd. ^e	1120	Corr. of above and from diamnized gelatin ^k
1250	Estimated ^d	1160	Conductivity ^l
1063	Electrometric titration ^e	1135	Calcd. ^m
839	Catalytic action ^f	1180	Electrometric titration ⁿ
885	Electrometric titration ^g		

^a Manabe and Matula, *Biochem. Z.*, **52**, 369 (1913).

^b Procter, Ref. 2c.

^c Bracewell, Ref. 3d.

^d Lloyd, *Biochem. J.*, **14**, 147 (1920).

^e Lloyd and Mayes, *Proc. Roy. Soc.*, **B93**, 69 (1922).

^f Wintgren and Kruger, *Kolloid-Z.*, **28**, 81 (1921).

^g Wintgren and Vogel, *ibid.*, **30**, 45 (1922).

^h Oakes and Davis, *J. Ind. Eng. Chem.*, **14**, 706 (1922).

ⁱ Loeb, Ref. 2a.

^j Hitchcock, *J. Gen. Physiol.*, **4**, 733 (1922).

^k Hitchcock, *ibid.*, **6**, 95 (1923).

^l Ref. *h*, p. 201.

^m Greenberg and Schmidt, *Proc. Soc. Exptl. Biol. Med.*, **21**, 281 (1924).

ⁿ Atkin and Douglas, *J. Am. Leather Chem. Assocn.*, **19**, 528 (1924).

Summary

1. A cell system is described which allows a close approximate measurement of diffusion potentials.

2. Reproducible diffusion potentials which show but small "time effects" have been measured with hydrochloric acid systems, hydrochloric acid-sodium chloride systems and hydrochloric acid-gelatin systems.

3. The reaction between hydrochloric acid and gelatin appears to be stoichiometric, purely chemical in nature.

4. A new and unusual method for determining the combining capacity of gelatin for hydrochloric acid is given. Four independent boundary measurements give the equivalent weight of gelatin as close to 1090.

Work of this nature is to be continued with di- and tri-basic acids and bases with gelatin, also for similar systems in which gelatin will be replaced by other proteins.

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DIFFUSION-POTENTIAL MEASUREMENTS APPLIED TO HYDROCHLORIC ACID-GELATIN SYSTEMS. II. THE COMPONENTS OF HYDROCHLORIC ACID-GELATIN SOLUTIONS¹

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A previous article² has shown that the equivalent weight of gelatin can be obtained from diffusion-potential measurements on hydrochloric acid-gelatin systems and that the reaction between hydrochloric acid and gelatin appears to be a stoichiometric one. This article explains the irregularities that were shown in some of the previous measurements³ and gives a more complete understanding of the conditions as existing in the various boundaries and solutions. All references to curves of Figs. 3 and 4 in this article refer to the same figures of the previous article.

The Effect of Uncombined Gelatin at the Diffusion Boundary

From comparison of curves in Fig. 3 with those in Fig. 4 it will be seen that the hydrochloric acid-gelatin solutions were not exactly similar to the hydrochloric acid-sodium chloride mixtures, as gelatin was added

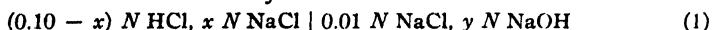
¹ The material presented in this article is constructed from a portion of the thesis submitted to the Graduate School of the University of Michigan by Egbert K. Bacon, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Ferguson and Bacon, *THIS JOURNAL*, **49**, 1921 (1927).

³ Portions of Curve $E_3(G)$ were concave upward, while similar portions of Curve E_4 were concave downward. Large "time effects" were observed in certain regions of curves $E_1(G)$, $E_2(G)$ and $E_3(G)$.

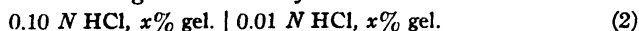
to the hydrochloric acid without regard to the amount needed for complete combination. (In fact, this amount was not known until after the experiments were carried out and the equivalent weight was determined.) Thus it happened that in many cases there was uncombined gelatin present in the acid-gelatin mixtures.

With the hydrochloric acid-sodium chloride mixtures free sodium hydroxide was never present. If sodium hydroxide had been added to the 0.01 *N* hydrochloric acid after complete neutralization had occurred (which corresponds to the regions beyond the maximum point *b* on Curve E_2), the condition at the boundary would have been

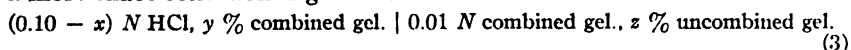


At such a diffusion boundary there is a new source of potential, that between *x* *N* hydrochloric acid and *y* *N* sodium hydroxide which, according to Planck,⁴ would be largely indeterminate because chemical action between sodium hydroxide and hydrochloric acid takes place at the boundary.

This appears to be similar to the condition which resulted in the *b c* region of Curve $E_2(G)$. The point *b* on the curve corresponds to a condition of complete combination between gelatin and 0.01 *N* hydrochloric acid so that instead of writing the boundary as



a more exact condition is given as



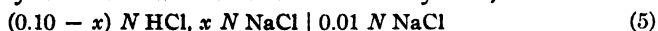
Thus, there was free hydrochloric acid and uncombined gelatin in contact at the boundary, until complete combination between the 0.10 *N* hydrochloric acid and gelatin had occurred, that is, a concentration of 10.9% of gelatin.

"Corrected" Curve for Boundary $E_2(G)$

If the above is the explanation of the real conditions existing at the contact boundary in the region *b c* of Curve $E_2(G)$, then a boundary such as



should correspond more nearly to the condition of the same region on curve E_2 of the hydrochloric acid-sodium chloride system,



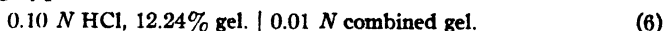
Accordingly, boundaries such as that given in (4) were measured. The results of these "corrected" measurements are given in Fig. 1 A, corresponding to 1.75, 4.37, 8.74 and 10.49% gelatin.

The path of the curve *b'c'* between 1.09% of gelatin and 10.9% of gelatin is now concave downward, the same as in Curve E_2 . It converges to the same point *c'*, as does Curve $E_2(G)$, when complete combination

⁴ Planck, *Wied. Ann.*, **40**, 561 (1890).

between 0.10 *N* hydrochloric acid and gelatin has taken place (10.9% of gelatin). This is further proof that the equivalent weight of gelatin is close to 1090, as shown in the previous article.

To show that uncombined gelatin present in the left-hand side of the boundary would have no appreciable effect on the potential after all of the free hydrochloric acid had combined with the gelatin, a boundary of the following type was measured.



This should give a potential similar to a boundary such as



since there is no free hydrochloric acid present in either system, but only combined and uncombined gelatin.

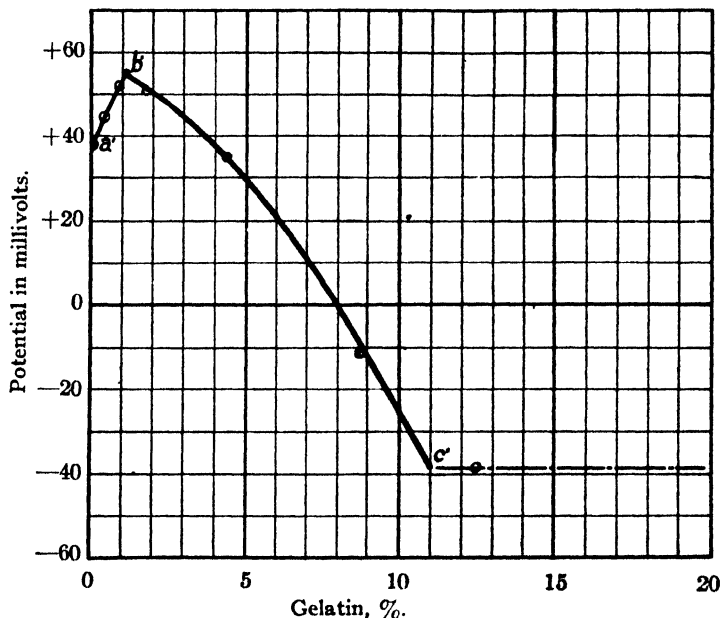


Fig. 1A.— $E_2(G)$, $0.01 \text{ } N \text{ HCl} + x\% \text{ gelatin} \mid 0.01 \text{ } N \text{ HCl} + y\% \text{ gelatin}$, where x varies from 0 to 10.9 and y varies from 0 to 1.09.

The potentials of these two boundaries were -37.69 mv. and -39.79 mv. , respectively. This close agreement shows that an excess of gelatin beyond the amount required for complete combination with the acid present has no appreciable influence on the diffusion potential.

The Function of Free Hydrochloric Acid and Uncombined Gelatin at the Diffusion Boundary

From these considerations it seems clear that the difference in observed potentials, as shown by Curves $E_2(G)$ and $2E_2(G)$, between points b

and c and b' and c' is a function of the concentration of free hydrochloric acid on one side of the boundary and the concentration of the uncombined gelatin on the other. It is the presence of these components on opposite sides of the contact layer that is the cause of the differences in diffusion potentials.

This is illustrated more conclusively by the following considerations. Any point on the $b'c'$ region of Curve $2E_2(G)$ represents the boundary condition as

$$(0.10 - x) \text{ N HCl, } y \% \text{ combined gel. } | 0.01 \text{ N combined gel.} \quad (8)$$

If z per cent. of iso-electric gelatin were added to the 0.01 N combined gelatin, any change resulting in the diffusion potential would be caused by the effect produced by the introduction of this excess of iso-electric gelatin. This is exactly the conditions that are represented in the region $b c$ of Curve $E_2(G)$, only it gives the results of proportionally increasing amounts of uncombined gelatin in contact with decreasing amounts of hydrochloric acid. If one of these factors is kept constant, the effect produced by changing quantities of the other can be observed. A boundary of the type

$$0.10 \text{ N HCl, } 1.75\% \text{ gel. } | 0.01 \text{ N combined gel., } x\% \text{ uncombined gel.} \quad (9)$$

illustrates such a condition. Boundaries of this nature were measured.

The solution in the left-hand side contained 1.75% of gelatin in 0.10 N hydrochloric acid or 0.084 N hydrochloric acid plus combined gelatin. The composition of this solution was kept constant. Varying quantities of iso-electric gelatin (which remained in the uncombined state) were added to the combined gelatin solution on the other side of the boundary.

The results of these measurements are given graphically in Fig. 2A, Curve 2(G)A. The potential is plotted as a function of the value of x , and the values of x used are 0, 0.66, 1.53, 4.15, 5.03 and 11.25. The curve appears to reach a limiting value at a potential around +15 mv. Concentrations of gelatin beyond 5 or 6% produce little effect.

Curve 2(G)B represents a boundary of the type

$$0.10 \text{ N HCl, } 5.24\% \text{ gel. } | 0.01 \text{ N combined gel., } x\% \text{ uncombined gel.} \quad (10)$$

This is similar to Boundary 9 but represents a lower starting point on $b'c'$, that is, where the free hydrochloric acid on the left-hand side of the boundary has the lower concentration, 0.052. The values for x are 0, 4.15 and 5.9. Concentrations of gelatin beyond 4% show little effect on this boundary.

Curve 2(G)C shows the results when the free acid has the still lower concentration, 0.0084 N . Constancy in potential is reached between 1 and 2% of gelatin.

Curve 2(G)D shows a condition of constancy when there is no free hydrochloric acid left. Any concentration of gelatin now has no appreciable effect on the potential.

To show further the difference between the effect of combined and uncombined gelatin the following boundary was measured,

$$0.10 \text{ N HCl, } 1.74\% \text{ gel.} \mid 4.37\% \text{ solution combined gel.} \quad (11)$$

in which one solution represents 1.75% of gelatin in 0.10 N hydrochloric acid and the other a 4.37% solution of *combined* gelatin, based upon the combining weight 1090 for gelatin. The value -39.19 mv. was obtained for the potential of this boundary. A similar boundary which contained 4.37% of *iso-electric* gelatin in 0.01 N hydrochloric acid gave a value of -8.61 mv.

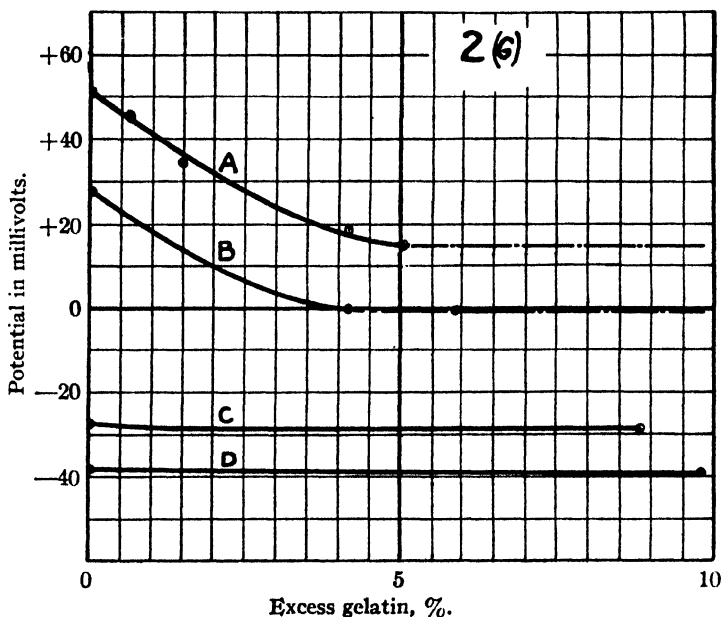


Fig. 2A.—The influence on diffusion potentials when uncombined gelatin is on one side of the boundary and free HCl on the other. Curve A, 1.7% gelatin, 0.084 N HCl; B, 5.2% gelatin, 0.052 N HCl; C, 10% gelatin, 0.008 N HCl; D, 10.9% gelatin, 0.000 N HCl.

Conclusions

The importance of defining hydrochloric acid-gelatin solutions in terms of free acid, combined and uncombined gelatin, is shown in these experiments. This can be done only if the stoichiometric character of the gelatin-acid combination is admitted and the equivalent weight of gelatin known. The understanding of the conditions existing in these hydrochloric acid-gelatin solutions and the cause of the observed potentials become clear when the following assumptions are made.⁵

- (1) Iso-electric gelatin combines stoichiometrically with hydrochloric

⁵ These are essentially the same as those of Loeb and his co-workers.

acid, at least between concentrations of 0.10 *N* and 0.01 *N*. Other interpretations of the curves which have been discussed could hardly lead to other conclusions. Five independent boundary measurements establish the equivalent weight of gelatin as close to 1090.

(2) Iso-electric gelatin, although considered neutral, is able by its amphoteric character to combine with hydrochloric acid much in the same manner as hydrochloric acid combines with sodium hydroxide. A highly ionized salt, gelatin chloride, is formed which is dissociated into a gelatin cation and a chloride anion.

From a consideration of these assumptions the diffusion potentials of hydrochloric acid-gelatin systems become understandable. When the components of the solutions are gelatin chloride (combined gelatin) and free hydrochloric acid, the observed potentials are very much the same as if the components were hydrochloric acid and sodium chloride. The introduction of any uncombined gelatin at one of the diffusion boundaries where free hydrochloric acid is present results in interaction between hydrochloric acid and gelatin at the boundary layer, with the formation of gelatin chloride. Thus the diffusion layer would be largely indeterminate and the potential would have no specific value or precise meaning. Examination of the experimental data and curves prove this, as erratic results were obtained whenever free hydrochloric acid and uncombined gelatin were at the boundary. This is in accord with Planck's views that a diffusion potential which results at a boundary where there is chemical action is largely indeterminate.

Summary

Important conclusions resulting from this investigation may be summarized as follows:

1. The components of hydrochloric acid-gelatin solutions should be defined in terms of free acid, combined and uncombined gelatin.
2. Diffusion potentials of hydrochloric acid-gelatin systems are only understandable if the hydrogen chloride-gelatin combination results in the formation of highly-ionized gelatin chloride.

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A NEW TYPE OF ROTATING ADIABATIC CALORIMETER. - THE SURFACE ENERGY AND HEAT OF SOLUTION OF SODIUM CHLORIDE. II

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In a previous paper¹ a method was described for determining the surface energy of a solid by measurement of the difference between the heat of solution of the solid in a coarsely crystalline and in a finely divided condition. The calorimeter used for this purpose had a rather serious defect in that the salt was exposed to the action of water vapor before solution was effected. A modified form of this calorimeter was therefore constructed, in which this defect was remedied; and in this paper an account of the work done with this calorimeter will be described. The heat of solution of finely divided sodium chloride has been again determined, this time directly; the results substantiate those obtained before. The area of the finely divided salt has been measured with more precision by the use of two different methods, and a more accurate value for the surface energy of solid sodium chloride thereby attained. With this calorimeter the heat of solution of the coarsely crystalline sodium chloride has been determined at 20° over the whole range of concentrations. Comparative agreement between duplicate experiments was obtained to better than 0.05% for concentrations above 10%. The heats of solution at 25° determined in the previous paper were corroborated, and from the temperature coefficient of the heats of solution the specific heats of sodium chloride solutions were calculated with high accuracy.

The main features of the former calorimetric apparatus are embodied in the present form and their description will not be repeated here. For a complete description of the apparatus, method of procedure, the precautions and corrections necessary, etc., the reader is referred to the first paper. The silver calorimeter vessel was, however, completely remodeled, and its description follows.

Description of Calorimeter

The calorimeter (Fig. 1) was a rotating type, cylindrical in shape and of the same exterior dimensions as the previously used calorimeter, so that it could be substituted in place of the old calorimeter and used with the same copper jacket, radiation thermel and axle as before. It differed in this respect, that the salt was placed in a separate receptacle which was covered by a lid so that the salt was protected from water vapor. For proper manipulation it was found necessary to be able to remove

¹ Lipsett, Johnson and Maass, *THIS JOURNAL*, 49, 925 (1927).

this receptacle from the calorimeter and for this purpose one end of the calorimeter was made removable.

As before, the calorimeter was constructed of sterling silver sheet. The open end of the calorimeter was flanged with a rim A of silver 3 mm. thick. This was closed by a disk of silver sheet B, which carried the supporting axle. A stout ring of brass C was made to press the silver disk tightly against the flange by means of ten brass screws running into the flange. The flange was previously coated with a thin film of vaseline. This gave a water-tight seal which was never found to give trouble and which allowed the easy introduction and removal of the box, D, which contained the salt. This box is shown separately in Fig. 1, c and d as it appears when removed from the body of the calorimeter. To enable it to be inserted into the calorimeter without jarring, and to hold it in position once inserted, a "runway" was constructed inside the calorimeter.

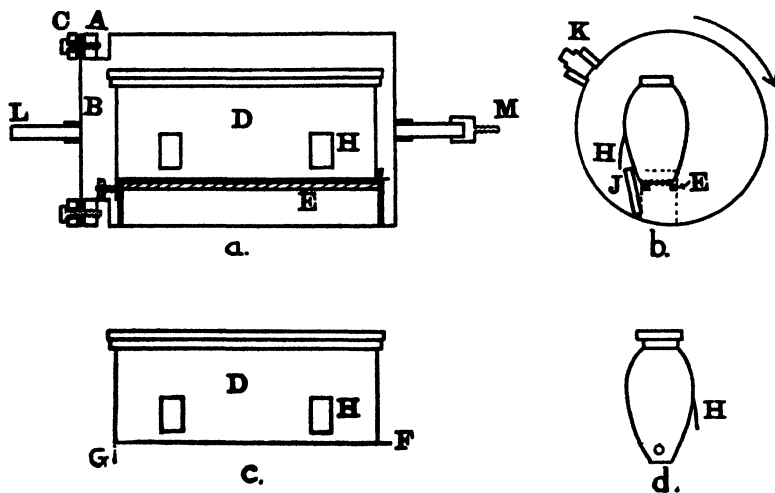


Fig. 1.

This was made of the same material as the rest of the calorimeter but is shaded in the diagram to differentiate it from the box. It consisted of two silver bars, E, soldered at each end to vertical pieces of silver sheet, which were in turn soldered to the wall of the calorimeter. The vertical sheet near the closed end of the calorimeter contained a slot into which fitted a projection F from one end of the box, while the other vertical sheet bore a small threaded rod which fitted into a hole in a projection G at the other end of the box. A small nut on the threaded rod served to hold the box in position. The top of the box was flanged and ground plane. A single piece of silver, $62 \times 11 \times 1.7$ mm., ground plane on one side, served as a lid. On rotating the calorimeter, the lid fell off and solution of the salt took place as before. To give an air-tight seal between the lid and the box, the flange of the box was coated with Glycoline. A film of vaseline, although preferable as a seal, caused the lid to adhere so strongly that it did not fall off on rotation. Even with glycoline, a lighter lid did not fall off on rotation.

It was found that if the lid were left free to slide about at random in the box during rotation, a rather large amount of heat was generated by friction, enough to cause a rise in the temperature of the calorimeter, containing 50 cc. of water, of about 0.0005° per minute. Small projections H were, therefore, soldered to the box, which trapped the lid after the first revolution of the calorimeter and prevented it from moving about

subsequently. The direction of rotation is indicated by the arrow in the diagram and the position of the trapped lid is shown at J. The lid, when so caught, acted as a baffle plate and caused more efficient mixing during the rotation, with the development by friction of only one-third of the heat generated when the lid was free to move about.

It will be noticed that the box is situated a little to one side in the calorimeter. This enabled a large quantity of water to wash in and out of the box on each revolution, thus increasing the speed of mixing.

The opening, K, for the water was so placed that there was no risk of wetting the lid of the box when the water was introduced. A silver plug closed this opening, as before.¹ The supporting axles, I, and M, were constructed similarly to those in the previous calorimeter.

Other Parts of the Apparatus

Only one change was made in the remainder of the apparatus. This consisted in the addition of a small tube from the copper jacket to the atmosphere, which enabled the air in the space between the calorimeter and the surrounding jacket to be kept at atmospheric pressure. Previously, the only tubes leading from the jacket to the outside were the tube containing the thermel lead wires and the tube through which the axle passed. The former was impervious to the passage of air since it had been filled with paraffin wax. The latter was found to be air-tight when the calorimeter was at rest, the vaseline used as lubricant acting as a seal, but on rotation the movement of the axle apparently offered means for the slow passage of air. This affected the calorimetric determinations in the following way. The temperature of the room might be, say 15° when the calorimeter was put in position and the outer jacket clamped on. If the calorimeter were later warmed to 25°, the air enclosed in the air gap would exert a pressure slightly higher than atmospheric but would not be able to expand. When the calorimeter was rotated, however, it would be able to escape and its expansion would produce a cooling effect. To prevent this, the air in the air gap was, therefore, opened to the atmosphere after the calorimeter had been brought to the temperature at which the run was to be made.

Procedure

A weighed quantity of salt was put into the box, the flange of the box was covered with a film of glycoline, and the box and contents were then allowed to stand in a desiccator over phosphorus pentoxide for two hours. The lid was put on the box while it was still enclosed in the desiccator, so that the box was filled with perfectly dry air. The box was then slipped into the calorimeter, the flange of the calorimeter was coated with vaseline, the end screwed on and a weighed amount of water run in. The procedure then followed the same course as described for the previous calorimeter.

Corrections

The corrections applied were the same as those used previously, with two additions. A correction was made for the heat capacity of the gly-

coline and the vaseline. The amounts of these substances used were practically the same in all the experiments, namely, 0.016 g. of glycoline and 0.035 g. of vaseline for which a total heat capacity was estimated of 0.02 cal.

The other correction necessary was due to the evaporation of water vapor into the dry air of the box when the lid fell off on rotation. This correction became large when only a small amount of salt was present in the box and was one of the chief reasons for making the box as small as possible. As a check on this correction, a blank run was carried out without using any salt, but filling the box with dry air as in the regular procedure and using 50 cc. of water in the calorimeter. On rotation a cooling effect was observed which, after allowing for heat generated by friction, amounted to 0.0030° . The theoretical lowering, as calculated, was 0.0029° .

The specific heat of the brass (64% copper, 36% zinc) used for parts of the calorimeter was taken as 0.0907 at 25° .² The weight of the brass parts was 20.39 g. The total weight of the sterling silver which made up the calorimeter was 133.94 g. Its specific heat was taken as 0.0581, as before.

Heats of Dilution.—It is obvious that this type of calorimeter can be used in determining heats of dilution as well as heats of solution. To illustrate this, some determinations were carried out with very dilute solutions of sodium chloride.

At 25° , 8.2 cc. of a 1.0% solution was placed in the small box and 41.3 cc. of water outside. On dilution, a rise in temperature of 0.0016° was obtained, of which 0.0011° was due to heat generated by friction during the rotation, leaving 0.0005° as the rise in temperature due to the reaction itself. To show the accuracy possible in measuring such small changes in temperature, the rise in temperature due to rotation was determined three times in this experiment, giving the values 0.0012, 0.0010 and 0.0011° .

Other heats of dilution were determined at 20° .

Comparison with Previous Results.—As a check on the apparatus and the previous work, some of the former determinations were repeated. Two runs were made with coarse salt at 25° . For a final concentration of 5.670%, the heat of solution was found to be -896.3 cal. per mole, as compared with -895.8 cal. found before. For a 4.620% solution, -928.1 cal. per mole was obtained as compared with -927.6 obtained previously. To substantiate the maximum in the heat of solution curve at 1%, a 1% solution was diluted to 0.166% and as was expected heat was evolved on dilution, giving $+23$ cal. per mole as the heat of dilution. As was just shown, the change in temperature on this dilution is very small and the

² Doerincel and Werner, *Z. anorg. allgem. Chem.*, 115, 1 (1921).

error in this heat of dilution may be 8 cal. per mole. In the previous work the heat of solution for a 1% solution was found to be -1015 cal. per mole, which gives -992 cal. per mole as the heat of solution for a 0.166% solution.

A determination was also made with some of the finely divided sublimed salt which had been used in the previous work. Its heat of solution was found to be 12.1 cal. per mole less than that of the coarse salt. The indirect measurements used previously gave a difference of 12.3 cal.

Heats of Solution of Sodium Chloride at 20°.—The results obtained for the heats of solution of sodium chloride at 20° are given in Table I.

TABLE I

HEATS OF SOLUTION OF SODIUM CHLORIDE AT 20°				
Concn., g. of NaCl per 100 g. of soln.	Sp. ht. of soln. at 20°, cal.	Wt. of H ₂ O used, g.	Approx. drop in temp., °C.	Heat of soln. per mole of NaCl, cal.
0.22	0.996			-1162
1.200	.9842	50	0.20	1158
1.200		50	.20	1152
4.620	.9438	41	.70	1042.8
4.620		41	.70	1043.6
8.085	.9092	50	1.17	915.5
8.085		50	1.17	914.6
10.732	.8850	50	1.41	819.3
10.732		50	1.41	818.9
13.946	.8572	50	1.65	710.7
13.946		50	1.65	710.9
19.540	.8173	50	1.90	560.2
19.540		50	1.90	560.0
25.791	.7838	32	2.00	460.8
25.791		32	2.00	460.6

The specific heats in Col. 2 were obtained from the same sources as in the previous paper. The calorie used throughout this paper is the 18° calorie and is taken equivalent to 4.1825 joules. Col. 3 gives the weight of water in which the salt was dissolved. The value for the 0.22% solution was obtained by diluting a 1.20% solution to 0.22%. For concentrations above 10%, the agreement between duplicate experiments is better than 0.05%, while for more dilute solutions, the agreement is of necessity not so exact.

The Specific Heats of Sodium Chloride Solutions.—The specific heat of a solution can be calculated very accurately from a knowledge of the temperature coefficient of the heat of solution, provided the specific heats of the pure solute and solvent are known. This is a direct application of the well-known Kirchhoff's Law, namely,

$$C - C^1 = (U^1 - U)/\Delta\theta \quad (1)$$

In this equation U represents the heat of reaction at θ° , U^1 , the heat of reaction at $(\theta + \Delta\theta)^\circ$, and C and C^1 represent the mean molal heat

capacities, respectively, of the reacting substances and of the products between the temperatures Θ and $(\Theta + \Delta\Theta)$.

In the present case, this equation may be written in the following form.

$$C_A + C_B - C_S = \Delta U/5 \quad (2)$$

C_A is the heat capacity of one mole of sodium chloride solid at 22.5° ; C_B is the heat capacity at 22.5° of the water in which it is dissolved, and C_S is the total heat capacity of the resulting solution, also at 22.5° . ΔU is the difference between the molal heats of solution at 25 and 20° .

The value for ΔU (disregarding all previous values used for the specific heats of sodium chloride solutions) may be expressed in terms of C_S and the actual experimental data obtained in determining the heats of solution at the two temperatures concerned. Knowing the values of C_A and C_B , the equation may be solved for C_S and the specific heat of solution thereby obtained. The details of such a calculation will not be given here since this method of obtaining specific heats has been described in detail by Richards and Rowe,³ who determined the specific heats of solutions from the temperature coefficient of the heats of dilution.

This calculation, although quite straightforward, is somewhat tedious in execution and the procedure, in the present case, was considerably simplified by obtaining the values for ΔU directly by difference from the heats of solution at 25 and 20° as already determined in this work. Although the calculation of these heats of solution involved the use of specific heats of the solutions as available in the literature, yet it will be seen that a fairly large error (say 0.3%) in these specific heats, although leading to an equal error (0.3%) in the heats of solution at 25 and 20° and thereby producing the same error in the value of ΔU , will finally lead to a much smaller error (less than 0.01%) in the specific heat of the solution then calculated according to Equation 2. If the calculated specific heat, thus found, differs by more than 0.3% from the value in the literature, the former may then be used to recalculate ΔU , and this, in turn, will give a more accurate value for the specific heat. In the present case, the values for the specific heats of sodium chloride solutions in the literature were found to be sufficiently accurate for the purpose, and the values of ΔU obtained by their use were used to calculate C_S . The mode of calculation is illustrated by the following example.

The specific heat of a 4.62% solution was taken as 0.9444 at 22.5° .^{3b} The molal heat of solution of sodium chloride at this concentration was found to be -928.1 cal. at 25° , and -1043.2 cal. at 20° . Substituting in Equation 2, the following result is obtained.

$$(0.208)(58.45) + (0.9993)(1206.7) - C_S = (1043.2 - 928.1)/5$$

or

$$12.16 + 1205.86 - C_S = 23.02$$

whence

$$C_S = 1195.0$$

³ (a) Richards and Rowe, *THIS JOURNAL*, **42**, 1621 (1920); (b) **43**, 770 (1921).

The first term represents the specific heat of solid sodium chloride at 22.5° multiplied by its molecular weight. It will be seen that an error of 1% in this heat capacity would lead, in this instance, to an error of only 0.01% in the value of C_S . The second term represents the specific heat of water at 22.5° multiplied by the weight of water in which the mole of salt was dissolved. This term is by far the largest of the three which result in the value of C_S and it is the most accurately known. The accuracy with which C_S may be determined is, therefore, limited by the accuracy with which the specific heat of water is known. The term on the right-hand side of the equation is $\Delta U/5$, and it is evident that an error of 1% in the evaluation of ΔU will result in an error of only 0.02% in the value for C_S . The weight of solution formed on solution of one mole of salt is 1265.2 g. which gives 0.9445 as the specific heat of the solution at 22.5° . The above analysis is given in detail to show that this method of determining specific heats, although indirect, is yet capable of yielding results of high accuracy.

The specific heats of sodium chloride solutions were then calculated according to the following procedure. The heats of solution at 25° and at 20° , obtained previously, were used, and values for ΔU were obtained by difference. Following the method suggested by Richards and Rowe, the values for ΔU were plotted against concentration and a smooth curve was drawn through the points. From the curve the values of ΔU at round concentrations were obtained and from these the specific heats of solutions at 22.5° were calculated, using Equation 2. The change in the specific heats with temperature was estimated from results given by Bousfield and Bousfield⁴ and the specific heats at 20° and at 25° thereby calculated. The specific heats so obtained are possibly accurate to 0.05%. The previous values for the heats of solution have all been recalculated, using these specific heats, since it was thought that more reliance could be placed on the newer values than on some of the older ones. In view of the increased accuracy afforded by these results, a more careful calibration of the platinum-resistance thermometer was made and showed that the previous results were 0.06% too low. The results were, therefore, increased by this amount. The heats of solution so obtained were plotted against concentration and the values at round concentrations found from the curve. These values, together with the values for the specific heats of the solution, as calculated from the temperature coefficient of the reaction, are given in Table II.

Among the most accurate determinations previously made of the specific heats of sodium chloride solutions are those by Richards and Gucker,⁵ and Richards and Rowe^{3b} at 18° . In Table III, their results

⁴ Bousfield and Bousfield, *Phil. Trans. Roy. Soc. (London)*, 218, 119 (1919).

⁵ Richards and Gucker, *THIS JOURNAL*, 47, 1876 (1925).

TABLE II

HEATS OF SOLUTION OF SODIUM CHLORIDE AND SPECIFIC HEATS OF SODIUM CHLORIDE SOLUTIONS AT 20 AND 25°

Concn. g. of NaCl per 100 g. of soln.	Heat of soln. cal. per mole of NaCl—		Specific heat, cal.—	
	20°	25°	20°	25°
0.200	—1163	— 993	0.9969	0.9963
.400	1168	1005	.9941	.9937
.600	1168	1010	.9915	.9911
.800	1166	1014	.9889	.9887
1.000	1162	1015	.9864	.9864
1.200	1156	1013	.9839	.9839
1.400	1150	1011	.9815	.9815
2.000	1133	1001	.9740	.9744
3.000	1100	974	.9625	.9629
4.000	1064.8	945.6	.9508	.9516
6.000	993.2	886.0	.9292	.9304
8.000	918.4	822.8	.9093	.9105
10.000	844.7	760.2	.8907	.8921
12.000	774.6	700.8	.8734	.8748
14.000	709.6	646.4	.8573	.8587
16.000	651.0	596.6	.8422	.8434
18.000	598.0	552.5	.8283	.8293
20.000	550.1	513.7	.8159	.8167
22.000	511.4	483.7	.8041	.8047
24.000	479.7	460.2	.7932	.7936
26.000	459.6	447.8	.7832	.7834

have been recalculated to 20° and compared with the values obtained in this work.

TABLE III

COMPARISON OF RESULTS WITH THOSE OF RICHARDS AND CO-WORKERS

Concn., g. of NaCl per 100 g. of soln.	Specific heat at 20°, cal.—	
	Richards and co-workers	The authors
0.8046	0.9889	0.9888
1.5964	.9794	.9792
3.1426	.9607	.9607
6.0939	.9285	.9283
11.488	.8782	.8777

The Heat of Solution of Finely Divided Sodium Chloride

Preparation of the Finely Divided Salt.—The salt was prepared by sublimation as before, but a new settling box was used (Fig. 2).

The dimensions of this box were 20 × 20 × 210 cm. It was divided into eleven compartments by baffle plates, as shown. These compartments gradually increased in size. The first, where the salt entered, was 5 cm. and the last 35.5 cm. long. The salt was sublimed from the platinum retort and the vapors were blown through this box. The coarser particles settled out in the first compartments and only the finest reached the last compartments. Glass plates on the bottom of each chamber received the salt as it fell, very little adhering to the walls. The front of the box, a glass plate, was removable. Strips of rubber (shaded in the diagram) were glued around the open

side of the box and down the edge of each baffle plate, and the glass was pressed against this by means of a wooden framework which was bolted to the box as shown.

Measurement of Size.—The size of the salt particles was obtained by two methods. In the first, the diameter of the particles was measured directly by the use of photomicrographs.⁶ In the second, the number of particles in a given weight of salt was found by direct count using a hemacytometer.⁷ In the latter procedure redistilled turpentine was used as a dispersion medium. Since the particles were not all of the same size, the relative distribution of the particles with regard to size was obtained from the photomicrographic measurements, and this, combined with the number of particles in a given weight, gave the average diameter per particle. The two methods gave results agreeing to within 0.1μ in the diameter of the average particle.

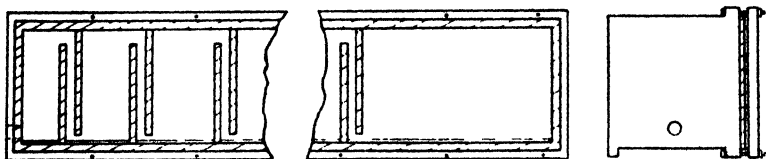


Fig. 2.

The Surface Energy of Solid Sodium Chloride

The heat of solution of the finely divided salt was measured at a concentration of 4.62% at 25°. The area of the salt was measured in the manner just indicated and the surface energy then calculated. The results are given in Table IV.

TABLE IV
SURFACE ENERGY OF SOLID SODIUM CHLORIDE AT 25°

Diameter of av. particle, ^a μ	Area per mole, sq. cm. $\times 10^{-8}$	Surface energy per mole, cal.	Surface energy per sq. cm., ergs.
1.00	1.62	15.3	395
1.16	1.40	13.6	406
1.14	1.42	12.1	356

^a This is not the arithmetical mean of the measured diameters but is a diameter such that, if the salt were composed of particles equal in size, which had this diameter, the area per mole would be the same as that actually occurring.

The figures in Col. 3 are the experimentally determined differences between the heat of solution of the coarse salt and the finely divided salt. The mean value for the surface energy of solid sodium chloride, as given above, is 386 ergs per sq. cm. at 25°.

Acknowledgment is made to the National Research Council of Canada for a grant to help in this work and for a studentship held by one of us, during the tenure of which this work was carried out.

⁶ Green, *J. Franklin Inst.*, 192, 638 (1921).

⁷ Kühn, *Z. angew. Chem.*, [1] 28, 126 (1915).

Summary

1. An improved type of rotating adiabatic calorimeter is described with which heats of solution or heats of dilution may be determined with high accuracy using only small quantities of material. The apparatus is constructed so that the solute, before solution, is not exposed to the vapor of the solvent.

2. Heats of solution of sodium chloride were determined at 20° over the whole range of concentrations.

3. An indirect but accurate method of determining specific heats of solutions is described, in which the specific heats are calculated from the temperature coefficient of the heats of solution.

4. From the heats of solution of sodium chloride at 20°, and those determined previously at 25°, the specific heats of sodium chloride solutions were calculated with an accuracy perhaps of 0.05% over the whole range of concentrations.

5. The heat of solution of finely divided sodium chloride was determined directly and from the difference between its heat of solution and that of the coarse salt, the surface energy of solid sodium chloride was calculated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF MERCURY VAPOR BY CHARCOAL

BY ALBERT SPRAGUE COOLIDGE

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In most arrangements for measuring gas adsorption, the adsorbent is constantly exposed to the vapor of mercury in pumps, manometers, etc., but it is tacitly assumed that no mercury is adsorbed. Sufficient grounds for this assumption are not evident. In general, vapors are more copiously adsorbed, the smaller the vapor pressures and molecular volumes of their liquids, the latter influence being particularly strong when the vapor is nearly saturated. On this basis, one would predict that mercury vapor would be more readily adsorbed than any other vapor or gas usually present, and that in the presence of liquid mercury at the same temperature, a sample of ordinary activated charcoal would take up several times its own weight. It is true that the pressure of mercury vapor in the system is generally very low; but this would merely delay, not prevent, adsorption, and in the course of a prolonged experiment there would be opportunity for considerable quantities of mercury to reach the adsorbent.

Certainly no such great adsorption occurs, and this is intimately connected with the fact that mercury does not wet charcoal. This means not that there is no attraction of the carbon surface for mercury atoms, but that this attraction is less than that of the free mercury surface, so that

the transfer of mercury from liquid to charcoal is endothermic. It should therefore occur, if at all, at high temperatures.

A preliminary investigation was made to see whether any adsorption could be detected at high temperatures. Three and five-tenths g. of activated coconut charcoal was suspended from a McBain¹ quartz spring balance, which had at 100° a sensibility of 5.45 mm. per g., and could be read, under the given conditions, to ± 0.005 mm., or about 0.3 mg. per g. of charcoal. At the higher temperatures used, the elasticity of the spring may have slightly increased, but the results did not seem to be sufficiently precise to make necessary the determination of a correction for this effect. Spring and load were hung in a wide glass tube closed at the top and connected at the bottom to a narrow vertical tube through which the system could be exhausted or mercury introduced from a leveling bulb. The wide tube and part of the narrow tube were kept at the desired temperature either by a vapor-bath (100, 218 and 306°) or by an electric furnace. The temperature of the latter was 480° as indicated by a pyrometer in which not much confidence was placed, although it was calibrated and found correct at 445°. A sharp temperature gradient thus existed in the narrow tube where it emerged from bath or furnace. In working at the higher temperatures, mercury was allowed to run in slowly until the meniscus reached a temperature at which the pressure of its vapor just balanced that due to the height of the leveling bulb. The pressure was estimated from the difference in levels, neglecting the expansion of the short column of heated mercury. It was found that the extension of the spring was proportional to the pressure, within the limits of error, showing that Henry's law holds, and that equilibrium was practically instantaneous. At the lower temperatures the pressure could not be safely found by this means; mercury was therefore allowed to enter the wide tube, and the pressure taken equal to the vapor pressure of mercury at the given temperature. No test of Henry's law could be made.

TABLE I
OBSERVED ADSORPTION OF MERCURY VAPOR

Temp., °C.	Press., mm.	Adsorption mg. per g.	P/a	Temp., °C.	Press., mm.	Adsorption mg. per g.	P/a
480	420	8.8	48	218	31.5	15.9	2.0
	730	16.2	45		31.5	16.8	1.9
	420	8.8	48			Av.	1.95
	220	4.5	49	100	0.28	2.7	0.11
		Av.	47			Av.	0.11
306	100	14.5	6.9				
	175	23.4	7.5				
	100	14.0	7.1				
	200	27.1	7.4				
		Av.	7.2				

¹ McBain and Bakr, *THIS JOURNAL*, 48, 690 (1926).

The experimental results are displayed in Table I. Col. 3 shows the amounts adsorbed, in milligrams per gram of charcoal; Col. 4 gives the ratio of pressure to amount adsorbed. Assuming Henry's law to be valid at all temperatures, this may also be regarded as the isostere for a constant concentration of 1 mg. per g. of charcoal.

In Fig. 1, the logarithms of the average values of P/a are plotted in the usual manner against the reciprocal temperatures, and fall as well as could be expected upon a straight line, the 1 mg. isostere. On the basis of Henry's law, other isosteres have been calculated and plotted, as well as the vapor pressure of liquid mercury. The slope of the isosteres leads

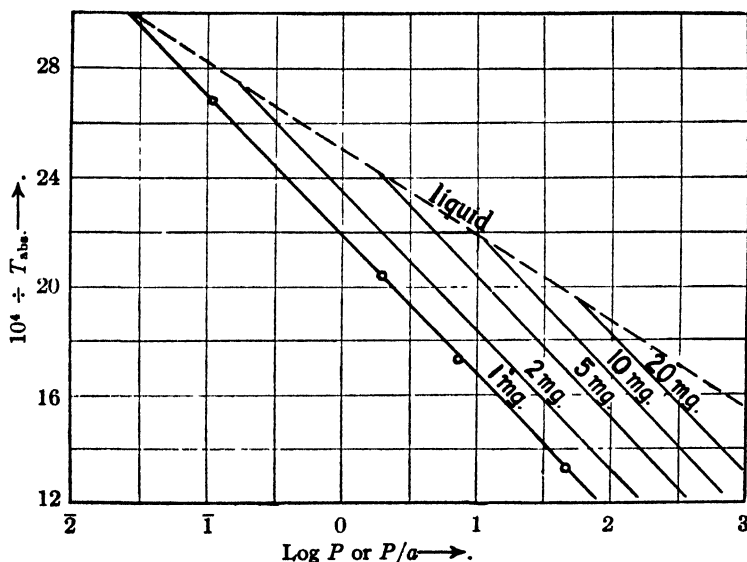


Fig. 1.

to a calculated heat of adsorption of 8900 calories per mole, which is much less than the heat of evaporation, 13,000 calories. While the transfer of mercury from gas phase at constant pressure to charcoal is exothermic and favored by low temperature, the transfer from liquid mercury to charcoal is seen to be indeed endothermic, consuming some 4000 calories, and taking place more readily at higher temperatures. The situation is similar to that which I found to exist in the case of ice and charcoal,² and is precisely analogous to the retrograde solubility of certain liquid pairs. It does not appear to have been previously described in the case of the adsorption of the vapor of a liquid.

If charcoal adsorbing a certain quantity of mercury is cooled, the vapor pressure of liquid mercury at the same temperature will fall faster than

² Coolidge, *THIS JOURNAL*, 49, 708 (1927).

the equilibrium pressure of the given mixture, and at a certain temperature will overtake it; at this temperature the system will be saturated, that is, in equilibrium with liquid mercury. The relation between this temperature and the amount adsorbed is shown in Table II (still assuming Henry's law). If the system is further cooled, its equilibrium pressure, though diminished, will now exceed the vapor pressure of the liquid, so that mercury will be desorbed and will collect as free liquid. The values in Table II therefore represent the maximum possible adsorption at the given temperatures. Evidently, there will be no significant adsorption under the conditions usually prevalent in work on other gases.

TABLE II
MAXIMUM ADSORPTION OF MERCURY VAPOR

Temp., °C.	Vap. press. of liq. Hg, mm.	P/a	α_{\max} mg. per g.	Temp., °C.	Vap. press. of liq. Hg, mm.	P/a	α_{\max} mg. per g.
20	0.0013	0.0042	0.3	220	33.7	2.04	16
60	.03	.026	1.2	260	98	4.0	24
100	.28	.11	2.5	400	246	7.2	34
140	1.85	.35	5.3	360	790	11.5	69
180	9.2	.89	10				

The heat of adsorption of mercury vapor, although less than its heat of evaporation, is still greater than the heat of adsorption of many true gases, and mercury vapor might therefore well be able to displace such gases from charcoal. This may be the explanation of a phenomenon which was repeatedly observed. When coconut charcoal which had been only briefly evacuated was treated with mercury vapor for three minutes, a considerable quantity of permanent gas was found in the system after all of the mercury had been condensed out. The same effect was obtained with sugar charcoal which had adsorbed formic acid, and had been only briefly evacuated. In this case the gas was doubtless carbon monoxide. The amount of gas evolved was much greater than would have come off spontaneously in a vacuum in the same time. In both cases the effect ceased when the charcoal had been subjected to prolonged evacuation.

Summary

Charcoal has been found to adsorb small amounts of mercury vapor at high temperatures. The amount adsorbed decreases with rising temperature when the vapor is kept at constant pressure, but increases with rising temperature when the vapor is kept saturated. The heat of adsorption is smaller than the heat of evaporation. At room temperature the adsorption is negligible.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A NEW ABSOLUTE MANOMETER FOR LOW PRESSURES

BY WORTH H. RODEBUSH AND CURTIS C. COONS

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The mercury manometer, including its more refined form, the McLeod gage, is preëminently the best type of manometer for measuring pressures below one atmosphere. It cannot be used, however, with gases which react with or dissolve appreciably in mercury, nor with gases which condense at the temperature at which the manometer is maintained, and the temperature range of operation is limited by the physical properties of mercury. The glass diaphragm manometer as developed by Daniels¹ and others is highly satisfactory at pressures above 10 mm. and such a manometer has recently been used in this Laboratory with success at 300°. In order to secure accuracy at low pressures, however, the glass diaphragm must be made so thin that it is too fragile for practical use. Various other ingenious forms of manometers have been devised, such as the Knudsen gage, Pirani gage and numerous types of ionization gages.² They all appear to be unsatisfactory, however, in that they are either difficult to operate or that they are not absolute but must be calibrated for each particular gas, which means that some other manometer must be used ultimately.

In connection with problems in this Laboratory, a manometer was needed which could be used for the measurement of very low vapor pressures of substances at any temperature and also for the measurement of thermal transpiration effects at low pressures. Such a manometer has been developed. It is essentially an absolute manometer which can be constructed of a single material resistant to corrosive gases (for example, Pyrex or silica glass) and which can be used at any temperature that the material will withstand. The pressure range is substantially that of the McLeod gage.

The construction of the manometer is shown in Fig. 1. D is a disk of graphite, the lower surface of which is ground to seat on the ground end of the glass tube. B is a small bob of soft iron, enclosed in glass, and A is an

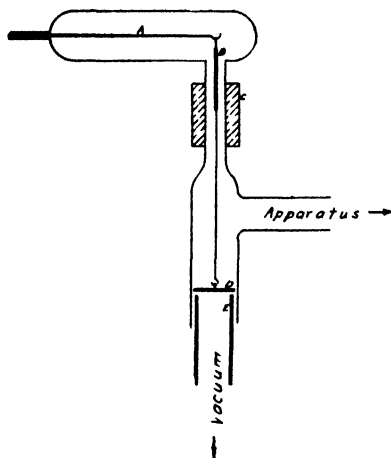


Fig. 1.

¹ Daniels and Bright, *THIS JOURNAL*, **42**, 1131 (1920).

² For a discussion of various types of manometers see Dushman, *High Vacuum*, *Gen. Elec. Rev.*, Schenectady, 1922.

arm made from a quartz fiber by which the system is suspended. C is a coil through which a current is passed to bring an electromagnetic traction on B. When the disk is seated on the tube at low pressures the leakage is slight and a nearly perfect vacuum may be maintained in the tube E while pressure equilibrium is attained above.

In operation sufficient current is passed through the coil to seat the disk firmly on E and time is allowed for pressure equilibrium to be established.

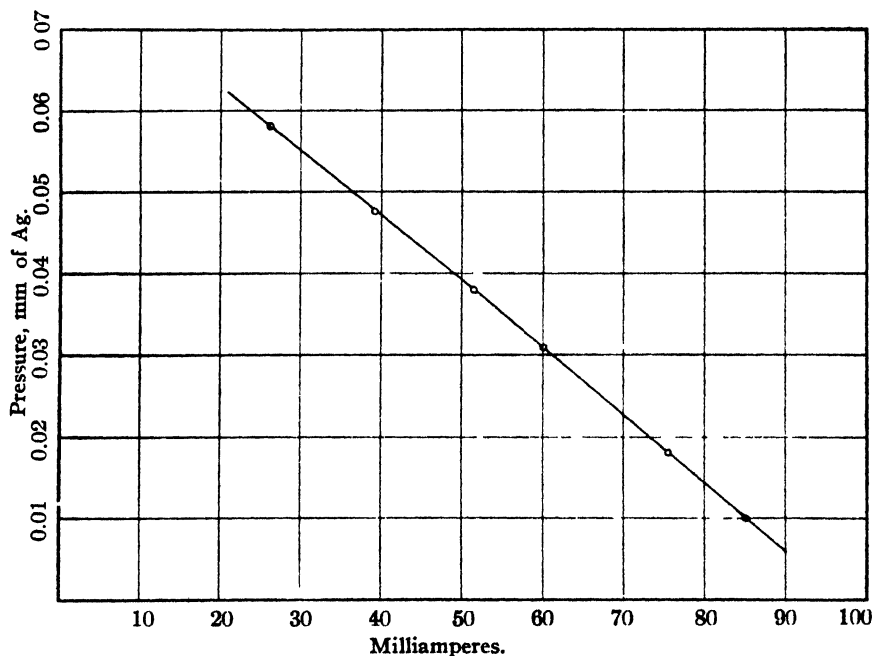


Fig. 2.

The current is decreased until the disk rises from its seat on the end of the tube. At this point the apparatus functions as an electromagnetic balance. The upward pull of the bent arm A is equal to the weight of the system plus the pressure of the gas plus the electromagnetic force. The current at which the disk begins to rise from its seat is easily determined because as soon as the disk rises slightly the gas flows into E and the pressure is equalized above and below the disk so that what is observed is a sudden rise of the disk to a height of nearly a millimeter above its seat. It was feared that irregularities in the seating of the disk or sticking might cause irregular behavior but no such difficulty was experienced. The current value for the balance at a given pressure is highly reproducible.

The disk D as constructed has an area of about 3 cm², and a pressure of 0.01 mm. exerts a downward pull of about 40 mg. so that it is not difficult to get sufficient sensitivity. While the manometer can be calibrated ab-

solutely by loading the disk with weights, it is more convenient to check it against a McLeod gage using air in the apparatus. The calibration curve is shown in Fig. 2. The curve is nearly linear but there are several effects which might cause a slight curvature.

For use at higher temperatures a furnace is placed around the tube in the neighborhood of D. For some purposes it may be desirable to interchange the connections to pressure and vacuum and invert the disk D and its seat.

The "zero point" of the apparatus will change somewhat with temperature but it can always be checked against a vacuum. The manometer is, of course, not suitable for use where the escape of gas from the apparatus must be avoided.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY OF THE
UNITED STATES BUREAU OF SOILS]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND MIXTURES OF THESE GASES AT 0° AND PRESSURES TO 1000 ATMOSPHERES.

A CORRECTION

BY EDWARD P. BARTLETT

RECEIVED JUNE 17, 1927

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A gage of the dead-weight type was used in the determination of the pressures recorded in a recent publication¹ concerning the compressibility of hydrogen, nitrogen and their mixtures.

An accurate calibration of the gage, made possible through recent acquisition of new equipment, shows that it was correct to within 0.1% at pressures to 100 atmospheres. At pressures of 200 atmospheres and above, an unsuspected error has been introduced, through the use of an incorrect ratio for the multiplying power of a lever attached to the gage only at these higher pressures. The maximum error in published results is 0.62% at 200 atmospheres, and becomes less at higher pressures.

The corrected results follow. The table number refers to the corresponding table in the original paper.

At pressures to 100 atmospheres the corrected results agree with those of Holborn and Verschoyle to within a maximum difference of 0.26% in the case of pure hydrogen and within 0.11% in the case of pure nitrogen. At 200 atmospheres the agreement with Amagat's results is almost exact. The maximum deviation from Amagat's results above 200 atmospheres is 0.34%. Corrected results for the three gas mixtures agree with those of Verschoyle at pressures to 100 atmospheres to within 0.10%. At 200 atmospheres the later results are larger by a maximum of 0.4%.

¹ Bartlett, *THIS JOURNAL*, 49, 687 (1927).

CORRECTED COMPRESSIBILITY FACTORS, p_v/p_0v_0 , FOR HYDROGEN, NITROGEN, AND FOR MIXTURES OF HYDROGEN AND NITROGEN AT 0.0°

At 0° and 1 atm., $p_0v_0 = 1$

TABLE III			TABLE V		
Press. atm.	Hydrogen Bartlett	Nitrogen Bartlett	25:75 H ₂ :N ₂ Bartlett	50:50 H ₂ :N ₂ Bartlett	75:25 H ₂ :N ₂ Bartlett
50	1.0337	0.9846	1.0036	1.0185	1.0266
100	1.0665	0.9846	1.0185	1.0426	1.0575
200	1.1383	1.0392	1.0784	1.1107	1.1283
300	1.2099	1.1380	1.1668	1.1938	1.2036
400	1.2827	1.2589	1.2712	1.2877	1.2896
600	1.4267	1.5253	1.5026	1.4849	1.4602
800	1.5723	1.8021	1.7400	1.6897	1.6335
1000	1.7148	2.0694	1.9707	1.8948	1.8053

TABLE IV

CORRECTED, OBSERVED (o) AND CALCULATED (c) COMPRESSIBILITY FACTORS (p_v/p_0v_0) AND OBSERVED DENSITY (d) FOR HYDROGEN, NITROGEN AND THEIR MIXTURES

At 0° and 1 atm., $p_0v_0 = 1$											
Press. atm.	H ₂ , %	100	88.5	75.4	55.1	45.9	34.1	26.0	13.7	6.1	0
	N ₂ , %	0	11.5	24.6	44.9	54.1	65.9	74.0	86.3	93.9	100
1	o	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	c
	d	0.0898	0.2233	0.3754	0.6110	0.7179	0.8548	0.9489	1.0917	1.1799	1.2507
	
50	o	1.0337	1.0318	1.0270	1.0199	1.0174	1.0101	1.0051	0.9958	0.9905	0.9846
	c	1.0336	1.0316	1.0276	1.0195	1.0161	1.0099	1.0048	0.9959	0.9896	0.9840
	d	4.3436	10.820	18.276	29.953	35.281	42.312	42.204	54.815	59.560	63.513
	
100	o	1.0665	1.0621	1.0580	1.0459	1.0398	1.0280	1.0201	1.0042	0.9948	0.9846
	c	1.0681	1.0638	1.0585	1.0466	1.0396	1.0290	1.0207	1.0061	0.9956	0.9867
	d	8.4200	21.024	35.482	58.418	69.042	83.151	93.020	108.71	118.60	127.03
	
200	o	1.1383	1.1295 ^a	1.1286	1.1162	1.1053	1.0928	1.0801	1.0619	1.0505	1.0392
	c	1.1390	1.1336	1.1280	1.1135	1.1045	1.0911	1.0804	1.0621	1.0495	1.0388
	d	15.777	39.539	66.524	109.47	129.90	156.44	175.70	205.61	224.63	240.70
	
300	o	1.2099	1.2072	1.2037	1.1990	1.1870	1.1760	1.1682	1.1546	1.1456	1.1380
	c	1.2137	1.2074	1.2059	1.1951	1.1879	1.1770	1.1684	1.1543	1.1448	1.1369
	d	22.266	55.492	93.561	152.87	181.44	218.06	243.68	283.65	308.98	329.71
	
400	o	1.2827	1.2842	1.2892	1.2898	1.2845	1.2755	1.2720	1.2659	1.2645	1.2589
	c	1.2839	1.2853	1.2869	1.2869	1.2822	1.2761	1.2719	1.2656	1.2616	1.2585
	d	28.003	69.553	116.47	189.49	223.56	268.07	298.40	344.96	373.24	397.39
	
600	o	1.4267	1.4422	1.4597	1.4810	1.4855	1.4951	1.5029	1.5149	1.5228	1.5253
	c	1.4281	1.4420	1.4585	1.4829	1.4890	1.4976	1.5042	1.5153	1.5227	1.5291
	d	37.765	92.899	154.31	247.53	289.96	343.04	378.82	432.38	464.89	491.98
	
800	o	1.5723	1.5975	1.6325	1.6804	1.6925	1.7198	1.7365	1.7671	1.7831	1.8021
	c	1.5723	1.5987	1.6301	1.6789	1.6958	1.7191	1.7365	1.7650	1.7838	1.7997
	d	45.691	111.82	183.96	290.88	339.33	397.62	437.16	494.23	529.37	555.21
	
1000	o	1.7148	1.7551	1.8037	1.8776	1.9039	1.9386	1.9667	2.0193	2.0436	2.0694
	c	1.7165	1.7554	1.8017	1.8749	1.9026	1.9406	1.9688	2.0147	2.0449	2.0708
	d	52.867	127.23	208.12	325.41	377.06	440.93	482.48	540.63	577.36	604.87
	

^a This result appears to be about 0.5% low. No adequate explanation can be given. It was the average result of five independent, closely checking experiments.

The magnitude of the corrections precludes the necessity of resubmitting graphical representation of the results shown in Figs. 1 to 3. Corrected values for the constants in the equations of state follow.

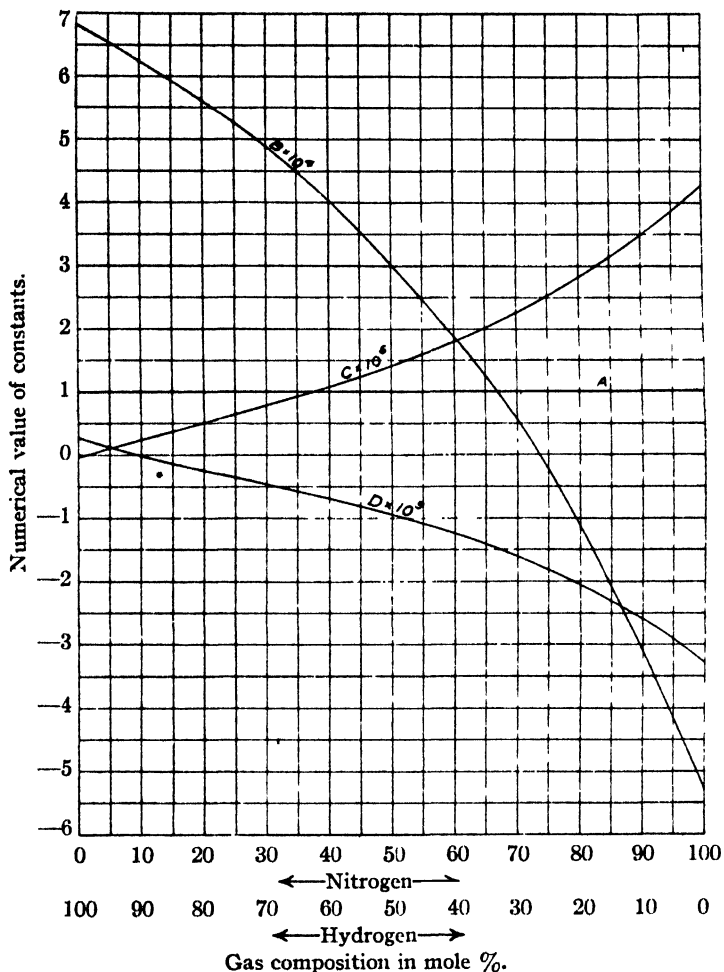


Fig. 4.—Numerical values of constants for use in calculation of compressibility factors of nitrogen, hydrogen and their mixtures to 400 atmospheres' pressure at 0°; $p/p_0 v_0 = A + Bp + Cp^2 + Dp^3$.

TABLE VI

VALUES OF CONSTANTS IN EQUATION OF TYPE 7 FROM OBSERVED DATA				
Constant	a	b	c	d
B	6.810×10^{-4}	-5.245×10^{-6}	-2.508×10^{-8}	-4.371×10^{-10}
C	-3.487×10^{-8}	$+2.914 \times 10^{-8}$	-1.488×10^{-10}	$+2.885 \times 10^{-12}$
D	2.564×10^{-10}	-3.072×10^{-11}	$+3.086 \times 10^{-13}$	-3.562×10^{-15}

Equation 9 $A = 1.2839 + (1.2084 \times 10^{-4})x$

Equation 10 $B = (7.211 \times 10^{-4}) + (5.322 \times 10^{-6})x + (1.0562 \times 10^{-8})x^2$

Equation 11 $A = 1.2585 + (5.155 \times 10^{-4})(100-x)$

Equation 12 $1/B = (1.3128 \times 10^3) - (7.153)x + (1.416 \times 10^{-2})x^2$

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF
LEHIGH UNIVERSITY]

CALCIUM NITRATE. I. THE TEMPERATURE-COMPOSITION RELATIONS OF THE BINARY SYSTEM CALCIUM NITRATE-WATER

BY WARREN W. EWING, NORMAN L. KREY, HARTLAND LAW AND ELHEIM LANG

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Calcium nitrate crystallizes from water solutions, forming crystals of tetrahydrate, trihydrate, dihydrate or anhydride. If the solution is seeded with a crystal of cadmium nitrate tetrahydrate, a β form of the tetrahydrate may be obtained.

Bassett and Taylor¹ and Taylor and Henderson² have investigated the temperature-composition relations of this system by means of the solubility method. They find that the tetrahydrate melts at 42.7°, the β -tetrahydrate at 39.6° and the trihydrate at 51.1°, and that the dihydrate crystals are in stable equilibrium with the saturated solution only between 48.4° and 51.3°. At this latter temperature a transition takes place, the anhydride and water being formed. They also report a cryohydric temperature at -28.7° and eutectic formation between the tetra-trihydrates and the tri-dihydrates. They remark that the freezing-point method gives anomalous results.

In some work on the vapor pressure of this same system one of the authors³ found, when crystals of the tetrahydrate are dehydrated in a vacuum at 35°, that they did not pass into the lower hydrated or anhydride crystalline forms, but that a solution phase began to appear. This behavior could not be explained by the then existing temperature-composition diagram. The following investigation was undertaken to complete the diagram. We have verified the data of the above investigators, except in the region of the dihydrate curve, and have extended the diagram into the metastable region. The freezing-point method has been used throughout.

Experimental Method

The calcium nitrate used and the method of analysis were the same as described in our vapor-pressure investigation.³ Crystals of tetrahydrate were made by drying the moist crystals over 60 per cent. sulfuric acid in a vacuum desiccator to constant weight. The anhydride was prepared in a similar manner, using phosphorus pentoxide as the drying agent. The various concentrations were made by mixing either water and tetrahydrate, or anhydride and tetrahydrate. By heating the latter mixture

¹ Bassett and Taylor, *J. Chem. Soc.*, 101, 576 (1912).

² Taylor and Henderson, *THIS JOURNAL*, 37, 1688 (1915).

³ Ewing, *THIS JOURNAL*, 49, 1963 (1927).

to 70° and stirring for some time, the anhydride could be brought into solution. All mixtures were analyzed after their freezing points had been determined.

The method of determining the freezing point of the solutions was essentially that of Lidbury,⁴ who has recommended a modification of the usual procedure for viscous solutions, in which equilibrium is attained slowly and in which, therefore, there is a considerable change in concentration before equilibrium is reached. He insulated the freezing tube with thick layers of cotton after crystallization had started, in order to prevent loss of heat to the surroundings.

The authors accomplished this same result by having the bath of the ordinary Beckmann apparatus consist of a vacuum tube with dilute sul-

TABLE I
TEMPERATURE-COMPOSITION RELATIONS

Ca(NO ₃) ₂ , % ^a	Temp., °C.	Solid phase
12.5	— 4.7	Ice
22.9	— 9.0	Ice
33.2	—16.1	Ice
46.2	—15.3	Tetrahydrate
52.0	+7.4	Tetrahydrate
59.9	30.2	Tetrahydrate
62.2	35.0	Tetrahydrate
66.2	40.5	Tetrahydrate
68.3	42.4	Tetrahydrate
69.5	42.7	α-Tetrahydrate (F. p. of compound)
69.5	39.7	β-Tetrahydrate (F. p. of compound)
69.8	42.7	Tetrahydrate
70.7	42.4	Tetrahydrate
Eutectic	42.6	Tetra-Trihydrate
71.3	42.5	Tetrahydrate
71.8	42.2	Tetrahydrate
73.4	40.9	Tetrahydrate
Eutectic	39.6	Tetra-Dihydrate
75.25	51.1	Trihydrate (F. p. of compound)
76.0	51.1	Trihydrate
76.0	48.1	Dihydrate
76.3	36.4	Tetrahydrate
76.3	50.8	Trihydrate
76.7	35.6	Tetrahydrate
76.7	49.8	Dihydrate
76.7	50.8	Trihydrate
Eutectic	50.6	Tri-Dihydrate
Transition	51.6	Di-Anhydride
Eutectic	32.7	Tetra-Anhydride
Eutectic	49.8	Tri-Anhydride

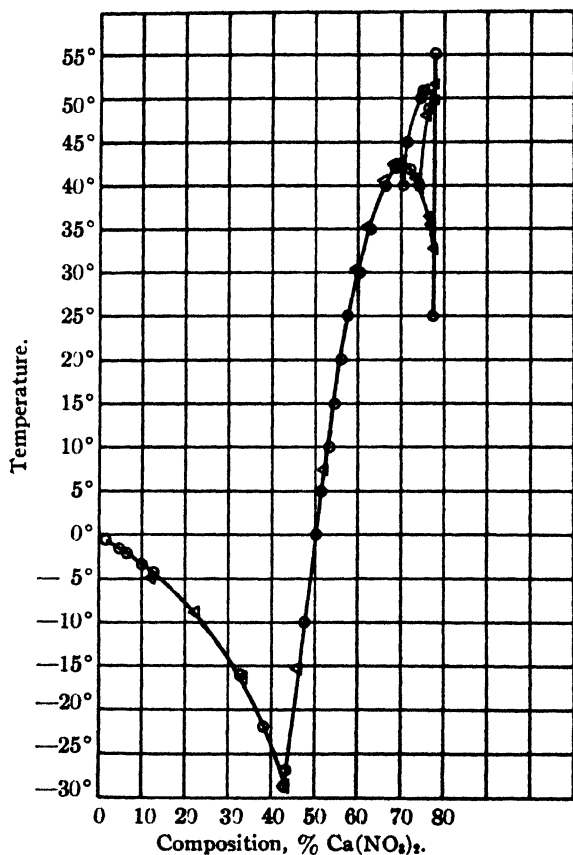
^a % = g. Ca(NO₃)₂ per 100 g. of solution.

⁴ Lidbury, *Z. physik. Chem.*, 39, 453 (1902).

furic acid for the liquid. Electrodes consisting of loops of copper wire were placed at the top and the bottom. When crystallization started, the bath could be quickly raised, by means of the 110-volt alternating current, to within one degree of the temperature of the melt and could be maintained there. This gave almost adiabatic freezing conditions, and assured a maximum freezing temperature with a minimum change in concentration.

Freezing points and eutectic temperatures were determined by plotting time-temperature cooling curves.

The data obtained are tabulated in Table I.



○ Bassett and Taylor; △ Ewing, Krey, Law and Lang.
Fig. 1.—Freezing point-composition diagram of the system calcium nitrate-water.

Discussion of Results

The results are also expressed graphically in Figs. 1 and 2. For purpose of comparison, the results of Bassett and Taylor are included in these

diagrams. The metastable region is plotted on a large scale in Fig. 2 for the sake of clearness, and to facilitate discussion.

Ice Curve.—For saturated solutions containing up to 44% of calcium nitrate, ice is the solid phase.

Tetrahydrate Curve.—For saturated solutions more concentrated than the cryohydric composition, calcium nitrate tetrahydrate is the solid phase. These equilibria are illustrated by curve A,B,C,D (Fig. 2). For concentrations higher than the tetra-tri eutectic the solid phase is in a metastable condition. Between B and C the solution is supersaturated with respect to the trihydrate, and between C and D with respect to both the tri- and the dihydrates. From vapor-pressure data we have found that this curve extends beyond D, in which region it is supersaturated with respect to the tri- and dihydrates and the anhydride.

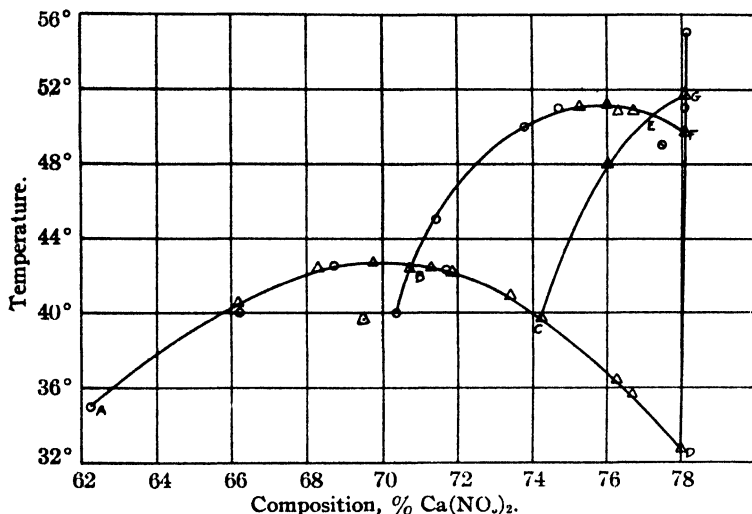


Fig. 2.—Detail of the freezing point-composition diagram of the system calcium nitrate-water. O Bassett and Taylor; Δ Ewing, Krey, Law and Lang.

Trihydrate Curve.—B,E,F is the curve for a saturated solution of calcium nitrate in equilibrium with solid calcium nitrate trihydrate. Below B it is supersaturated with respect to the tetrahydrate and between E and F with respect to the dihydrate.

Dihydrate Curve.—C,E,G is the curve for a saturated solution in equilibrium with solid calcium nitrate dihydrate crystals. The reaction $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$ represents the transition taking place at G (51.6°). Between E and C the solution is supersaturated with respect to the trihydrate. Vapor-pressure data show that this curve extends below C, in which region the solution is supersaturated with respect to both the tetra- and the trihydrates.

Anhydride Curve.—D,F,G is the saturated solution curve for the anhydride. It extends from below 25° up to its boiling point, 151°, at which temperature its concentration is 79% of calcium nitrate. The anhydride is in a metastable condition below the transition temperature, G.

β $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.—We have confirmed the existence of the metastable beta modification of the tetrahydrate by seeding a melt of tetrahydrate composition with a crystal of cadmium nitrate tetrahydrate. This gave a freezing point at 39.6°.

Types of Cooling Curves.—For any of the solutions having concentrations between about 70 and 78% several different time-temperature cooling curves are possible. Taking the 76% concentration as an example, four different curves have been obtained. They are as follows:

	F. p.	Solid phase	Eutectic	Solid phases
1)	51.1°	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	50.6°	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
2)	51.1°	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	49.8°	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2$
3)	48°	$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	39.6°	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
4)	36.8°	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	32.7°	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2$

Which of the four possible curves will be obtained depends upon some undetermined factor. Seeding with carefully prepared crystals apparently had little effect, sometimes one modification being obtained, sometimes another. Frequently, while one of the lower crystalline hydrates was crystallizing out in the metastable state, the temperature would suddenly rise, indicating a transformation to the stable modification. This usually occurred when the melt was nearly solid and was probably due to scratching the crystals with the stirrer.

Summary

1. The freezing-point method has been applied to determine the temperature-composition diagram of the binary system calcium nitrate-water.
2. A metastable region has been found and investigated. It lies between the concentrations of about 70 and 78% and between temperatures of 20 and 51°. In this region there are metastable eutectic mixtures containing tetra- and dihydrates, tetrahydrate and anhydride, and trihydrate and anhydride. The saturated solutions in this region are supersaturated with respect to various modifications and their solid constituents are in metastable conditions.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF
LEHIGH UNIVERSITY]

CALCIUM NITRATE. II. THE VAPOR PRESSURE- TEMPERATURE RELATIONS OF THE BINARY SYSTEM CALCIUM NITRATE-WATER

BY WARREN W. EWING

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In recent years considerable work has been published on the vapor pressures of hydrated inorganic salts. Three general methods have been used in obtaining the data. Washburn and Heuse¹ have published a critical study of the dynamic method as applied to the vapor pressure lowering of solutions. Baxter and Lansing² have applied this method in a study of the vapor pressures of crystals, obtaining accurate results. The procedure is to pass a known volume of dry air over the mixture of crystals and to analyze for its acquired water content. Carpenter and Jette³ have made, recently, a critical study of the static method and have applied it in determining the vapor pressures of hydrated crystals of various sulfates. In this method the substance is confined over one arm of a manometer and its pressure is compared with that of some known reference material.

Early measurements by these two methods gave conflicting results, but Menzies⁴ has made a critical comparison of the two, using cupric sulfate, and has pointed out that if proper precautions are observed they give concordant results.

Indirect methods have been investigated by Wilson⁵ and by Noyes and Westbrook.⁶ These consist in establishing vapor distribution equilibrium between the hydrates and some reference material; in establishing water distribution equilibrium between the hydrates and some liquid in which the salt is insoluble; and of various other ingenious devices.

The method used in this investigation was the so-called dynamic method developed by Smith and Menzies.⁷ It seems to be rather a static method since the substance is maintained at equilibrium pressure over a confining liquid and the vapor pressure is read from a manometer under static conditions. Derby and Yngve⁸ and Edgar and Swan⁹ have recently used this

¹ Washburn and Heuse, *THIS JOURNAL*, **37**, 309 (1915).

² Baxter and Lansing, *ibid.*, **42**, 419 (1920).

³ Carpenter and Jette, *ibid.*, **45**, 578 (1923).

⁴ Menzies, *ibid.*, **42**, 1951 (1920).

⁵ Wilson, *ibid.*, **43**, 704 (1921).

⁶ Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

⁷ Smith and Menzies, *ibid.*, **32**, 1448 (1910).

⁸ Derby and Yngve, *ibid.*, **38**, 1439 (1916).

⁹ Edgar and Swan, *ibid.*, **44**, 570 (1922).

method with excellent results. A voluminous bibliography is contained in the references mentioned above.

Although extensive investigation has been carried out in this field, a rather limited amount of reliable data has accumulated, due largely to the fact that most of the recent work has been concerned primarily with a study of methods. In the data available the vapor pressures of most systems are given at only one temperature, usually in the neighborhood of 25°. Vapor pressure-temperature relations have been investigated for only a few systems. These are either of simple type or for systems having such high melting or transition temperatures that only the partial vapor pressure-temperature diagrams have been investigated. The calcium nitrate-water system lends itself admirably to a complete investigation for the following reasons:

The complete temperature-composition diagram¹⁰ has been worked out. The lowest temperature of this system is the cryohydric temperature at -28.7°. The vapor pressure of this point is the same as the known vapor pressure of ice at that temperature. Three hydrates and an anhydride exist. The tetrahydrate melts at 42.7° and the trihydrate at 51.1°. The dihydrate has a transition temperature at 51.6°. There are five eutectics, the lowest being at 32.7°. Complete vapor-pressure data can, therefore, be obtained for all mixtures of crystal systems and for all saturated solutions of the hydrates by making measurements through the temperature range 20 to 60°. Calcium nitrate is very soluble in water, 77.3% at 25° and 79% at its boiling point, 151°. The anhydride is the solid phase at these concentrations. All of the concentrated solutions can be supercooled to very low temperatures. Complete vapor-pressure-temperature data for solutions up to 79% can thus be obtained by measuring the vapor pressures between 20 and 60° and by determining the boiling points of the solutions. The vapor pressure-temperature relations for the three types of systems: mixtures of hydrated crystals, saturated solutions and solutions of various concentrations, give a complete equilibrium diagram for the binary system calcium nitrate-water.

Experimental Methods

Materials.—The calcium nitrate was prepared by treating a high grade of calcium carbonate with nitric acid and was subsequently crystallized out. This material was recrystallized as tetrahydrate, eight times, from water.

Apparatus.—The apparatus used was essentially the isoteniscope of Smith and Menzies,¹¹ with the following modifications. The bulb for the material had a volume of about 25 cc. To insure concentration equilibrium in the solutions an electromagnetic stirrer was enclosed. The bulb also had a side tube for ease in filling and in sealing it on to the isoteniscope. Cottonseed oil was used as the confining liquid. It is superior to a mineral oil in that it wets glass better than water does. The water vapor bubbling

¹⁰ Ewing, Krey, Law and Lang, *THIS JOURNAL*, 49, 1958 (1927).

¹¹ Smith and Menzies, *ibid.*, 32, 1448 (1910).

through the oil had no tendency to condense on the glass in the capillary tube, whereas when a mineral oil was used drops of water frequently formed on the walls of the glass capillary and blocked it up. The large vacuum and air reservoirs were eliminated.

In securing pressure equilibrium small quantities of air were admitted by means of a straight stopcock with a solid core. This core had a small cavity which carried air from the atmosphere side to the vacuum side. The pressure in the system could be lessened in small increments by quickly turning the stopcock between the system and the Cenco Hyvac pump.

Pressure was measured by comparing the mercury level in the manometer tube with that in a barometer tube of the same diameter (1 cm.). Both tubes were connected with the same mercury reservoir at their lower ends. A complete vacuum was assured above the barometer liquid by having it attached to a McLeod gage which registered a pressure of 0.018 mm. of mercury. The difference in heights between the manometer and the barometer mercury was read by means of an accurately graduated brass cathetometer with a vernier reading to 0.05 mm. Readings were corrected to zero degrees. A mercury trap was used instead of a stopcock between the isoteniscope and the remainder of the system. This insured against leakage of air through periods of a month, which was the time required to complete the measurements for some of the systems.

The electrically controlled thermostat could be regulated to $\pm 0.05^\circ$. All temperature measurements were made with mercury in glass thermometers which were compared with a thermometer calibrated by the Bureau of Standards.

Analysis of Samples.—The samples were analyzed by placing them in weighing bottles overnight in an electric oven at 70° , which dried them to about 75% calcium nitrate. They were then cooled, seeded, crystallized and dried over phosphorus pentoxide in a vacuum desiccator, forming the anhydride. Constant weight was usually attained in five days. They were then dried for two weeks longer and check weighings made. All samples were analyzed in duplicate. This method was checked by means of the oxalate method and concordant results were obtained.

Procedure.—The usual procedure was followed in making the readings. Since the two most common criticisms of this method are that adsorbed air is not entirely removed and that equilibrium is difficult to obtain, these two points will be discussed.

When a solid phase is present in work of this type, a large amount of air is adsorbed on the surface. The finer the crystals, the greater is the surface, and consequently a larger amount of air is adsorbed. Most workers have assumed that the evaporation of water of crystallization from hydrated crystals effectually removes this adsorbed gas. Menzies,⁴ however, has demonstrated with cupric sulfate that there is a residual gas which is slowly evolved and that its pressure may amount to as much as 0.3 mm. In this work this adsorbed gas was eliminated by the initial treatment of the sample. The correct amounts of materials were placed in the tensimeter so that, at the lowest temperature measured, the system would be practically all crystalline with not more than one mm. of supernatant saturated solution. This was necessary in order to obtain concentration equilibrium quickly, since it was not possible to stir the contents. The temperature was then raised until but a few small crystals remained. While in this condition the tensimeter was evacuated, intermittently, until a large volume of water vapor had been removed. The

temperature was then lowered and the mass crystallized in contact only with solution and water vapor. This effectually eliminated adsorbed air. As conditions of greater solubility were reached in determining the vapor pressure-temperature curve of the saturated solutions, more water vapor was removed in order to maintain the above-mentioned relations between volumes of solid and saturated solutions. Finally, when proper concentrations existed, eutectic crystallization was induced, still in the presence only of solution and water vapor, and the vapor pressure-temperature curve for these mixtures of crystals was determined. In one case, that of the dihydrate-anhydride, measurements were made on an intimate mixture of dry crystals after they had been thoroughly evacuated to remove adsorbed air and the results checked those obtained by the above-mentioned preparation.

Pressure equilibrium between mixtures of hydrated crystals and water vapor is attained quickly or slowly according to some specific nature of the substance. By grinding the crystals together to form an intimate mixture equilibrium is hastened. Some hydrated crystals can be kept an indefinite length of time under conditions at which they would be expected to dehydrate. In this metastable condition a scratch will start dehydration. In our vapor-pressure measurements on the mixtures of crystals of the tetra- and dihydrates and of the tetrahydrate and the anhydride, the tetrahydrate was apparently in such a metastable condition. The above-described method of forming a mixture of the crystals by eutectic formation gives a very intimate mixture of the crystals. Pressure equilibrium was established within four hours. However, the final measurement was made only after 24 hours. The saturated solution required about the same time interval. Solutions, when only one phase was present, came to equilibrium in a half hour, but two hours were allowed before making the final measurement. Two points on each solution curve represent overnight time intervals.

Accuracy of Results.—The difference in heights of the mercury columns could be read to within 0.05 mm. of mercury. A variation of 0.05° in temperature at 60° gives, for the most dilute solution, a change in pressure of 0.3 mm., and for the most concentrated solution, a pressure change of 0.05 mm. At 20° these changes are respectively, 0.07 mm. and 0.01 mm. For mixtures of crystals and for saturated solutions the maximum variation, per change of 0.05° , is 0.05 mm. at the higher temperatures, and 0.01 mm. at 20° . Therefore, the change in pressure, due to variation in the temperature of the thermostat, is negligible except in the case of the dilute solutions at the higher temperatures. At these higher temperatures the most probable vapor pressures were determined by following the change in vapor pressure with the change in temperature as the heaters of the thermostat went on and off. The error here

is probably as great as 0.1 mm. The accuracy of the results is further attested by the fact that with but a half-dozen exceptions all points fall within 0.1 mm. of the plotted curves.

A preliminary test of the apparatus was made using cupric sulfate. The vapor pressure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ was found to be 7.8 mm. Menzies⁴ finds 7.80 mm. by the dynamic method and 7.74 mm. by the static method, while Wilson⁵ obtains 7.80 by an indirect method. Other investigators find values scattered from 7.0 to 8.5 mm.

A final check was made by determining the vapor pressure of water at 20, 30, 40, 50 and 60°. The results are within 0.1 mm. of those of Scheel and Heuse.

From the above considerations the author estimates a maximum error of 0.1 mm. in the results presented.

Boiling Points of Solutions.—The boiling points of the solutions were determined by the bulblet method of Smith and Menzies.¹² The bulb had a volume of 10 cc. and 3 to 5g. samples were taken. These samples were analyzed in the usual manner after the runs. Paraffin wax having a melting point of about 55° was used as the confining liquid. This was a convenient liquid because in removing the bulb from the bath some of the bath liquid always sucked back into it. This solidified and so permitted the removal of the uncontaminated solution for analysis. The temperature was maintained constant to within 0.1° by means of an electric coil and vigorous stirring.

The following boiling points for the various concentrations were obtained: 21.5% $\text{Ca}(\text{NO}_3)_2$, 102.1°C.; 32.1%, 104.1°; 51.1%, 111.8°; 60.5%, 119.6°; 69.9%, 132.0°; 75.0%, 142.8°; 77.4%, 147.3°. By plotting these data, boiling points for any concentration may be obtained. This gives the following boiling points for the concentrations for which solution vapor pressures were measured: 20.2%, 102°; 30.6%, 104°; 49.6%, 111°; 59.1%, 118.3°; 66.6%, 126.7°; 72.2%, 136.0°; 74.2%, 140.5°; 74.7%, 141.5°; 76.3%, 145.0°; 76.9%, 146.4°; 77.4%, 147.5°. At these temperatures the vapor pressures of these various solutions are 760 mm.

Gerlach¹³ gives results uniformly lower than these for concentrations above 50%. His results are evidently in error since he obtains the boiling point of 152° for a saturated solution containing 82% of calcium nitrate.

Discussion of Results

The vapor-pressure data obtained are tabulated in Tables I, II and III. For clearness of presentation and to facilitate discussion, the data are also plotted in the various curves. The reader should also refer to the temperature-composition diagram in the preceding article.

¹² Smith and Menzies, *THIS JOURNAL*, 32, 897 (1910).

¹³ Gerlach, *Z. anal. Chem.*, 26, 413 (1887).

TABLE I

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, CRYSTALS-SATURATED SOLUTION-WATER VAPOR

I. Crystal Phase, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$					
Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
0	2.7	39	19.5	38	8.6
5	3.9	40	19.7	37	7.75
10	5.2	41	19.7	36	7.0
15	6.9	42	19.3	35	6.4
20	9.4	42.5	19.0	34	5.75
25	12.0	42.5	15.5	32	4.7
30	14.9	42	13.8	30	3.9
35	17.7	41	12.25	25	2.4
36	18.2	40	10.9	20	1.5
37	18.9	39	9.5	15	1.15
38	19.3				

II. Crystal Phase, $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$					
Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
35	13.3	46	19.8	51	19.4
40	16.2	47	20.2	51	16.8
42	17.8	48	20.5	50.5	15.4
43	18.3	49	20.6	50	14.4
44	18.8	50	20.5	49	13.3
45	19.3	50.5	20.2		

III. Crystal Phase, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$					
Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
20	4.25	45	13.2	50	15.3
30	7.1	48	14.4	51	15.6
40	11.1	49	15	51.5	15.8

IV. Crystal Phase, $\text{Ca}(\text{NO}_3)_2$					
Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg.	Temp., °C.	V. p., mm. Hg
30	4.2	50	14.6	54	18.1
35	5.9	51	15.3	55	19.0
40	8.0	52	16.1	57	21.2
45	10.8	53	17.2	60	24.9
48	12.8				

TABLE II

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, MIXTURES OF CRYSTALS-WATER VAPOR

I. Crystalline Phases, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$					
Temp., °C.	V. p., min. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
20	3.0	37	11.7	40	14.8
25	4.5	38	12.5	41	15.8
30	6.8	39	13.7	42	16.9
35	10.0				

II. Crystalline Phases, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$					
Temp.	V. p.	Temp.	V. p.	Temp.	V. p.
20	2.8	35	8.0	38	9.8
25	4.0	36	8.6	39	10.6
30	5.7	37	9.2		

TABLE II (Concluded)

III. Crystalline Phases, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2$					
Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
20	2.0	25	3.0	30	4.1
IV. Crystalline Phases, $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$					
20	1.8	35	5.7	45	10.8
25	2.65	40	7.8	50.5	15.6
30	3.8				
V. Crystalline Phases, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2$					
20	1.5	38	6.2	48	12.4
25	2.2	40	7.1	50	14.4
30	3.3	45	10.1	51	15.3
35	4.9				

TABLE III

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, SOLUTIONS OF $\text{Ca}(\text{NO}_3)_2$ IN WATER-WATER VAPOR

Temp., °C.	V. p., mm. Hg													
	20 2%	30 6%	40 7%	50 1%	60 6%	72 2%	74.2%	74 7%	76 3%	76 9%	77 4%			
20	16.4	15.3	11.3	8.2	5.4	3.7	3.2	(3.05)	2.5	2.35	2.3			
30	29.9	27.6	20.6	15.1	10.4	6.9	6.0	5.8	4.0	4.6	4.5			
40	52.6	48.0	36.1	26.6	18.7	12.7	10.7	10.4	9.2	8.6	8.4			
50	86.8	80.2	61.3	45.3	31.6	21.9	18.9	18.0	16.2	15.1	14.8			
60	140.6	130.5	99.7	75.0	52.7	36.8	31.9	(30.0)	27.5	25.5	25.0			

* % = g. $\text{Ca}(\text{NO}_3)_2$ per 100 g. of solution.

Saturated Solution Curves.—In Fig. 1, A,A,A is the vapor pressure-temperature curve for a saturated solution in contact with crystals of the tetrahydrate; B,B,B the trihydrate; C,C,C the dihydrate; and D,D,D the anhydride. In each of these saturated solutions the same supersaturated conditions for the solutions and the same metastable conditions for the crystals prevail as described in the composition-temperature discussion in the preceding article.

On the curve for the saturated solution in contact with crystals of the tetrahydrate the vapor pressure rises rapidly with the temperature up to about 37°. At this temperature the rate of increase slows down, with rise in temperature, due to the increased solubility becoming the predominating factor. At 41° the vapor pressure even begins to decrease with rise in temperature until the melting point, 42.7°, of the tetrahydrate is reached. The reflex portion of the curve represents the saturated solution in unstable equilibrium with respect to the other crystalline forms. The initial region of this curve may be extrapolated to meet the vapor pressure of ice, 0.321 mm., at the cryohydric temperature, - 28.7°. This is permissible because at this condition ice, tetrahydrate, saturated solution and water vapor are in equilibrium and, therefore, the vapor pressure of the system is the same as the vapor pressure of any of the constituents. The curve for the trihydrate is similar to that for the tetrahydrate. The

dihydrate and the anhydride curves do not show a region of decrease in vapor pressure with increase in temperature. This is because the dihydrate reaches its transition temperature before its melting point is reached, and the saturated solution boils (151°) below the melting point of the anhydride. The vapor pressure of water above this solution should approach zero as the composition of the saturated solution approaches pure anhydride and the temperature approaches the melting point of the anhydride.

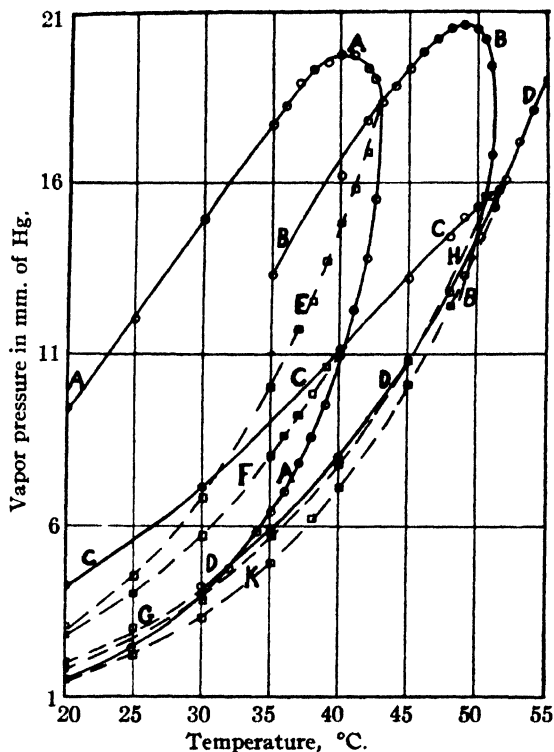


Fig. 1.—Vapor pressure-temperature relations for saturated solutions and for mixtures of hydrates of calcium nitrate.

Mixtures of Crystals.—At the temperatures at which the saturated solution curves meet, the pressure is the vapor pressure of the eutectic equilibrium for the four phases crystal + crystal + saturated solution + water vapor, except in the case of the dihydrate and the anhydride saturated solutions, where it is the vapor pressure of the transition equilibrium $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$. Here, too, the same four phases are present. At lower temperatures the saturated solution phase disappears and the vapor pressure is that of the mixture of two crystalline forms.

These conditions are represented by curve E, Fig. 1, for a mixture of tetra- and trihydrates; F for tetra-di-; G for tetra-anhydride; H for tri-di-;

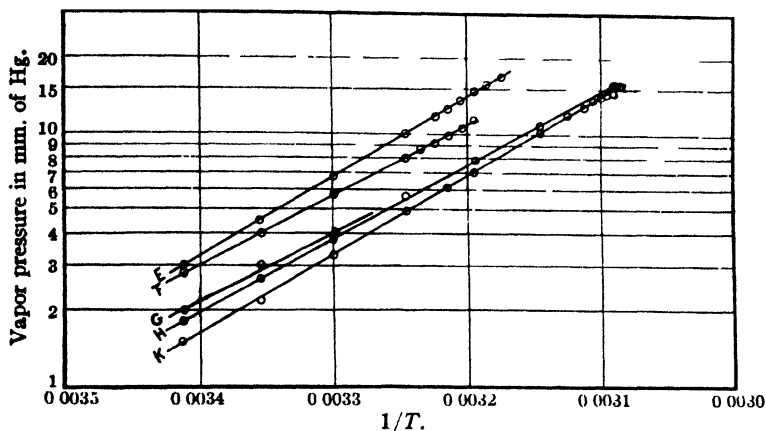


Fig. 2—Mixture of crystals.

and K for di-anhydride. The curve for the trihydrate-anhydride mixture was not determined. It would lie about 0.2 mm. above that for the di-

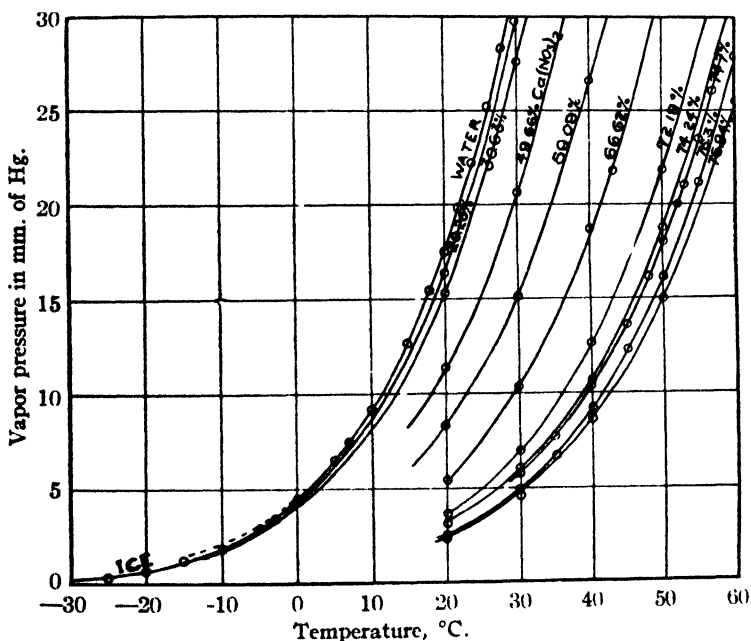


Fig. 3.—Vapor pressures of solutions of calcium nitrate in water.

hydrate-anhydride. This is but slightly greater than the experimental error of measurement.

In Fig. 2, the vapor pressure of these mixtures is plotted against the inverse of the absolute temperature, on a logarithmic scale for the pressure, the letters E, F, G, H and K having the same significance as above. Except for one point on the tetra-anhydride curve, all experimental values fall upon the straight lines. This is in agreement with the results of other investigators on this type of system.

Solution Curves.—Fig. 3 gives the vapor pressure-temperature relations of solutions of calcium nitrate in water for various concentrations from 20 to 77%. A solution of calcium nitrate saturated with the anhydride at 25° contains 77.3% of calcium nitrate. The vapor pressure data for water and ice are those of Scheel and Heuse.¹⁴

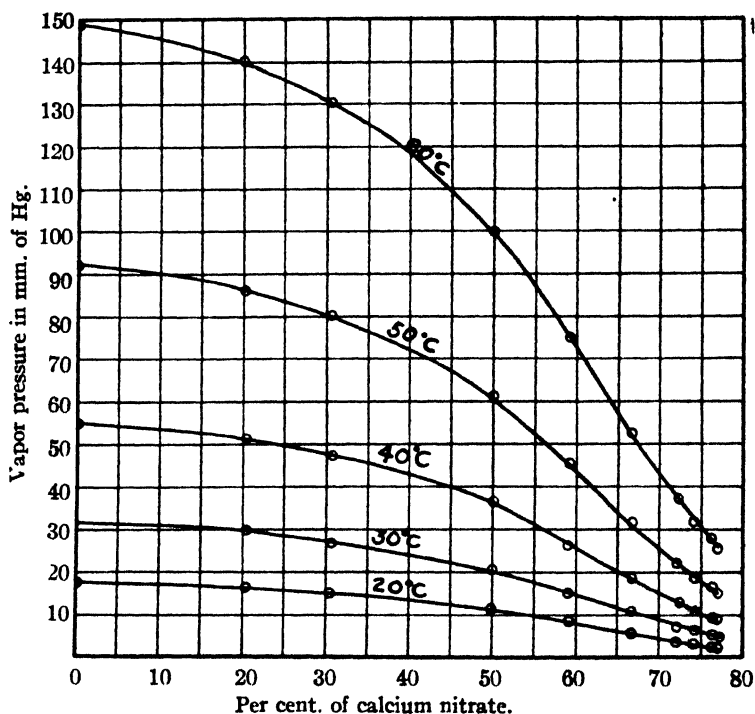


Fig. 4.—Vapor pressure-composition isotherms for calcium nitrate solutions.

The 20.2% and the 30.6% curves have been extrapolated to meet the ice curve at the temperatures at which they are in equilibrium with ice. If these data are plotted with the logarithm of the pressure against the inverse of the temperature as coördinates, apparently straight lines are obtained for temperatures up to 60°. The same holds for water. These lines are not parallel but converge in the direction of the higher temperatures. Above 60°, however, the value of $\ln P$ for water falls below

¹⁴ Scheel and Heuse, *Ann. Physik* [4] 29, 723 (1909); [4] 31, 715 (1910).

the straight line, the divergence increasing steadily up to its critical temperature. If values of the vapor pressure (760 mm.) at the boiling temperatures of these various solutions are plotted on this same diagram, these curves also show a change in slope similar to that of water.

Temperature-Composition Diagrams from Vapor-Pressure Data.—Fig. 4 contains vapor pressure-composition isotherms plotted from the solution data in Table III. From these curves it is possible to plot any number of additional vapor pressure-temperature curves for solutions. If a sufficient number of such curves are superimposed upon the saturated solution curves in Fig. 1, it is possible to obtain data for a complete temperature-composition diagram, at the vapor pressures of the systems, for this system. The point at which any given solution curve crosses any given saturated solution curve gives the composition and temperature data for that solution. Data obtained in this manner give a temperature-composition diagram which is, within experimental error, the same as Fig. 2 in the preceding article, with the additions that the unstable saturated solution curves extend beyond the various eutectics.

Thermal data for these systems are being measured in this Laboratory. Thermal data calculated from these vapor-pressure measurements will be presented when this work is completed.

Summary

Complete vapor-pressure-temperature relations of the binary system calcium nitrate-water have been determined. This involved measurements at various temperatures from 20° to the boiling points of the solutions, and for various concentrations from 20% to the saturated solution of the anhydride. The systems in this region contain dilute solutions and supersaturated solutions, stable and unstable saturated solutions, and stable and metastable mixtures of crystals.

In the mixtures of crystals, $\ln P$ is proportional to $1/T$. Solutions apparently obey the same law up to temperatures of about 60°.

Temperature-composition diagrams can be constructed from vapor pressure-temperature data.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE VAPOR PRESSURE OF THE SATURATED AQUEOUS SOLUTIONS OF CERTAIN SALTSBY H. GENEVA LEOPOLD¹ AND JOHN JOHNSTON

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In the course of an investigation of the absorption of water by various materials, it was necessary to maintain atmospheres of constant humidity, which is best achieved by the use of a saturated salt solution. A survey of the literature on the vapor pressure of saturated salt solutions showed the data to be incomplete and of insufficient accuracy for our purpose; for much of the work consists of single measurements at a single temperature, and in many cases the several results differ by far more than the supposed experimental error. We undertook, therefore, a redetermination of the vapor pressure of some saturated solutions over the temperature range 20 to 50°, and believe that the uncertainty in the final results is not greater than 0.05 mm.; the salts used were sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, potassium bichromate and, in addition, sodium chloride and potassium chloride together. Such data, apart from their practical utility, yield also a measure of the activity of both the salt and the water in these solutions, and this constitutes the best means of evaluating these quantities at temperatures other than in the freezing range of the solutions.

We have correlated our results with the data available on the vapor pressure of unsaturated solutions of the same salts by means of a sensitive method of plotting. This led us to observe that the vapor pressure of a saturated solution—presumably, therefore, also of some unsaturated solutions—attains to its final value only after the solution has been maintained at constant temperature for a period of 24 hours. This observation probably accounts for the lesser accuracy of many prior results, for it has been usual to record the pressure observed at the end of a period, at a given temperature, measured in minutes rather than in hours.

Experimental

The vapor pressure was measured directly, the form of apparatus used being that described by Johnston.² The essential feature is that between the bulb containing the solution and the main manometer, there is in a sort of double U-tube, a small mercury trap, the levels of which are adjusted by appropriate manipulation of stopcocks controlling the admission or extraction of air; after the whole apparatus has been thoroughly evacuated, this mercury is made the confining liquid and subsidiary manometer, and at pressures less than 60 mm. is the only manometer needed. The only modifications were the interposition of a bulb containing phosphorus pentoxide, to prevent access of

¹ From the dissertation presented to the Graduate School of Yale University, in June, 1926, by H. Geneva Leopold in candidacy for the degree of Doctor of Philosophy.

² Johnston, *Z. physik. Chem.*, **62**, 347 (1908).

water to the main manometer and the pump, and of a trap to prevent spattering of the solution over into the subsidiary manometer. The difference in level of the mercury columns was read by means of a depth gage,³ the vertical rod of which was set in bearings in a rigid brass frame; on its cross bar was mounted a small reading lens, at the center of which was glued a pointed piece of paper. When this is set up in front of, with a mirror at an equal distance behind, the manometer, the image of the paper point is in the plane of the manometer, and so errors due to parallax are avoided. With this simple form of cathetometer, the uncertainty in the readings is about 0.03 or 0.04 mm. The observed pressures were all reduced to their equivalent in terms of mercury at 0°.

The salt solution, previously heated to boiling, was introduced into the bulb, which was then sealed off; such air as had been retained by the solution was removed by continued pumping of vapor from the warm solution, this process being repeated until the observed final vapor pressure remained unchanged upon further pumping. The removal of the dissolved air is more difficult than we had anticipated; a period of 3 or 4 days is in many cases needed.⁴ Even so, when the temperature of the solution has been changed, the pressure does not attain to a new constant value until the lapse of several hours; consequently we use a thermometer and took readings, with frequent shaking of the solution bulbs, over a period of at least 24 hours. This gradual change to the equilibrium pressure, which may differ from the initial pressure by 0.2–0.3 mm., occurs after each evacuation of vapor from the solution, and is therefore due presumably to the slow equalization of some degree of undersaturation or supersaturation of the salt at the surface of the solution.

Each datum in Table I is the mean of 6 or more readings taken over an interval of at least 24 hours, and in many cases longer, during which the temperature was kept constant to $\pm 0.01^\circ$. The large number of observations made before we realized that a period of an hour at a given temperature is insufficient, have been omitted entirely; when plotted in the terms used in this paper, these points lie (along with those of previous workers) in a cluster so large that one could not determine in which direction to produce the curve.

TABLE I
THE OBSERVED VAPOR PRESSURES OF SATURATED AQUEOUS SALT SOLUTIONS

Temp., °C. <i>t</i>	Moles salt per 1000 g. water, <i>M</i>	Vapor pressure of water <i>p₀</i>	Vapor pressure of solution <i>p</i>	$\Delta = \frac{p_0 - p}{p_0 M}$
KCl				
21.42	4.664	19.14	16.23	0.03258
25.62	4.849	24.65	20.72	.03286
27.56	4.926	27.65	23.27	.03216
33.64	5.178	39.11	32.46	.03284
39.31	5.402	53.32	43.70	.03339
44.03	5.576	68.37	55.62	.03273
NaCl				
20.42	6.130	18.19	13.65	0.04073
25.49	6.148	24.45	18.35	.04057
29.96	6.167	31.75	23.80	.04060
36.92	6.201	46.86	35.03	.04070
40.55	6.220	56.96	42.54	.04070
50.00	6.277	92.51	68.84	.04077

³ Brown and Sharp depth gauge No. 605, with a range of 500 mm., capable of being read to 0.01 mm. Cf. Ferguson, *J. Wash. Acad. Sci.*, 10, 285 (1920). Another form is described by Lowry, *J. Opt. Soc. Am.*, 11, 645 (1925).

⁴ Cf. Lovelace, Frazer and Sease, *THIS JOURNAL*, 43, 102 (1921).

TABLE I (Concluded)

Temp., °C. t	Moles salt per 1000 g. water, M	Vapor pressure of water p_0	Vapor pressure of solution p	$\Delta = \frac{p_0 - p}{p_0 M}$
NaCl and KCl				
22.19	20.06	14.41
25.53	24.52	17.50
27.60	27.70	19.79
27.60	27.70	19.72
27.62	27.73	19.80
31.08	33.83	23.98
Na ₂ SO ₄				
20.83	1.427	18.44	16.01	0.09221
25.02	1.953	23.78	20.44	.07276
28.46	2.552	29.12	25.17	.05310
32.38	3.473	36.44	31.47	.03885
35.02	3.473	42.22	36.74	.03991
42.88	3.371	64.39	57.03	.03390
50.55	3.283	95.06	84.39	.03418
K ₂ SO ₄				
18.90	0.6256	16.37	15.91	0.04507
22.25	.6620	20.13	19.55	.04350
24.73	.6884	23.38	22.60	.04857
25.58	.6974	24.59	23.89	.04203
31.55	.7600	34.77	33.61	.04408
35.96	.8052	44.47	42.90	.04371
43.42	.8825	66.23	63.74	.04261
48.41	.9333	85.46	82.11	.04208
52.30	.972	103.60	99.13	.04444
K ₂ Cr ₂ O ₇				
23.66	0.482	21.92	21.43	0.04627
26.40	.545	25.93	25.30	.04522
32.82	.698	37.35	36.05	.04999
36.21	.790	45.08	43.42	.04672
40.85	.920	57.88	55.48	.04510
50.77	1.210	96.10	91.55	.03917

Table I, Col. 2 contains the molality (M) of the saturated solution at t , as derived from the "best" curve drawn through a large-scale plot of the solubility data available.⁵ Cols. 3 and 4 list the vapor pressure at t° of water⁶ (p_0) and of the solution

⁵ Some points on the curve chosen may be found in Table IV. The individual references are: Potassium chloride: Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Brönsted, *Z. physik. Chem.*, 80, 208 (1912); 82, 621 (1913); Andreae, *J. prakt. Chem.*, [2] 29, 456 (1884); de Coppet, *Ann. chim. phys.*, [5] 30, 426 (1883); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, 35, 345 (1883); Meusser, *Z. anorg. Chem.*, 44, 79 (1905); Foote, *Amer. Chem. J.*, 35, 238 (1906); Sudhaus and Miner, *Jahrg. Beil. Bd.*, 37, 18 (1914); Amadori and Pampanini, *Atti. accad. Lincei*, 20, II, 475 (1911). Sodium chloride: Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Andreae, *J. prakt. Chem.*, [2] 29, 456 (1884); Raupenstrauch, *Monatsh.*, 6, 563 (1885); Taylor, *J. Phys. Chem.*, 1, 718 (1897); Moller, *Pogg. Ann.*, 117, 386 (1862); de Coppet, *Ann. chim. phys.*,

(p), expressed in millimeters of mercury at 0° ; and the last column lists the molal relative vapor pressure lowering, calculated from these data, a quantity which is plotted against the molality in the figures.

A Graphical Method of Evaluating Vapor-Pressure Data on Solutions.—The accuracy of vapor-pressure data has commonly been estimated from their regularity; but this criterion fails in the presence of a constant, or regular, error such as the presence of air or the use of an inaccurate thermometer. A much better criterion is the ratio of the vapor pressure of the solution to that of water (solvent) at the same temperature; in other words, to compare the relative humidity (p/p_0) which is affected differently at different temperatures by a constant error in p . The use of this ratio also shows up chance errors in p —since p/p_0 must vary regularly with temperature—provided that the vapor-pressure curve of the solvent has been accurately determined. A still more sensitive criterion, since for most salt solutions p/p_0 is not far from unity, is $1 - p/p_0$ or $(p_0 - p)/p_0$, the relative lowering of vapor pressure; and if this quantity is divided by the molality (M), the relative molal lowering of vapor pressure (Δ) so derived is found to change quite slowly with change in the salt concentration. Therefore a plot, even on quite a small scale, of this function (Δ) against the molality shows up the degree of accuracy of the experimental results; indeed, with all except the very best data, the points are so scattered that one finds difficulty in deciding just how the curve should be drawn.

As an instance of the fact that Δ changes slowly with concentration, the values of Δ derived from the measurements of Lovelace, Frazer and Sease⁴ in solutions of potassium chloride above 1 M are as follows:

M	1.2461	1.5099	1.7072	1.9938	2.2450	2.4916	3.0017	3.5783	4.0070
$\Delta \times 10^4$	3159	3166	3167	3169	3173	3180	3200	3220	3233

This regularity, which shows that these results are accurate to 0.001 mm., as claimed by the authors, contrasts with the irregular values of Δ lying between 0.30 and 0.33 as derived from the work of other authors in this same range of concentration.

Let us now consider the effect of change of temperature upon the function [5] 30, 426 (1883); Gay-Lussac, *Ann. chim. phys.*, [2] 11, 310 (1819). Sodium sulfate: Richards and Yngve, *THIS JOURNAL*, 40, 164 (1918); Takenchi, *Mem. Coll. Kyoto*, 1, 249 (1915); Wuite, *Z. physik. Chem.*, 86, 349 (1914); Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, 35, 345 (1883); Loewel, *Ann. chim. phys.*, [3] 49, 50 (1857); Gay-Lussac, *Ann. chim. phys.*, 11, 312 (1819). Potassium sulfate: Berkeley, *Trans. Roy. Soc. (London)*, 203A, 189 (1904); Trevor, *Z. physik. Chem.*, 7, 468 (1891); Andrae, *J. prakt. Chem.*, [2] 29, 456 (1884); Tilden and Shenstone, *Proc. Roy. Soc. (London)*, 35, 345 (1883). Potassium dichromate: Koppel and Blumenthal, *Z. anorg. Chem.*, 53, 263 (1906); Kremers, *Pogg. Ann.*, 92, 499 (1854); Alluard, *Compt. rend.*, 59, 500 (1864); Sherrill and Eaton, *THIS JOURNAL*, 29, 1643 (1907); Le Blanc and Schmandt, *Z. physik. Chem.*, 77, 621 (1911).

⁴ Taken from the Reichsanstalt "Wärmetabellen," by Holborn, Scheel and Henning, 1909, Vieweg and Son, Braunschweig.

tion Δ . If we calculate, from measurements at a series of temperatures of the vapor pressure of a solution of constant composition, the values of Δ —or what suffices in this case, the relative humidity p/p_0 —we find that the values at adjacent temperatures differ by as much as those at the highest and lowest temperature. In other words, *within the accuracy of the data available*, the relative humidity—and hence Δ —may be regarded as independent of temperature. This is the principle, first stated by Princeps, commonly known as Babo's law;^{7a} and is equivalent to the statement that the activity of water in a solution of constant concentration is substantially independent of the temperature. It is quite clear, however, that if there were measurements of sufficient accuracy, on a solution of constant molality at a series of temperatures, we would observe a slight increase in relative humidity with increase of temperature.^{7b} This rate of increase would be parallel to the rate at which the average degree of "hydration" of the ions of the salt decreases with rising temperature, and it would seem that this trend should be most marked for those salts which ordinarily form the largest hydrates, a view which is substantiated by the results for sodium sulfate.

The fact that, for a solution of constant molality, the relative humidity, and hence the function Δ , is independent of temperature *within the limits of accuracy of existing data*, enables us to omit temperature from further consideration, and so to bring together on a single plane diagram all of the data upon solutions of a salt from freezing range to the boiling point of a saturated solution. On this diagram the coördinates are molality and Δ , the relative lowering of vapor pressure of water per mole of solute. In the few cases in which the vapor pressure of a single solution was measured at a series of temperatures, we used the average value of Δ ; in general, for a given value of M , there is available only a single value of Δ , but these may refer to quite different temperatures. This plot thus allows one to correlate results from various sources, to estimate their relative accuracy and to derive throughout the range of concentration definitive values of higher accuracy than have hitherto been available. It is much more sensitive than the method proposed by Bencowitz,⁸ namely, to plot $\log p/p_0$ against $1/T$; for on this basis he is able to represent by straight lines data which our figures indicate are of doubtful accuracy.

^{7a} Recent data which confirm this principle, *within the accuracy of the measurements*, are those on cane sugar solutions by Perman and Saunders (*Trans. Faraday Soc.*, **19**, 112 (1923)). This is further exemplified by a comparison of the work of Sidgwick and Ewbank (*J. Chem. Soc.*, **125**, 2268 (1924)) on solutions of potassium chloride, sodium chloride and potassium sulfate at 5°, with that of Tammann (*Ann. Physik*, **24**, 523, (1885)) on the solutions of these salts at 100°.

^{7b} See, for example, in the very recent results of Perman and Lovett (*Trans. Faraday Soc.*, **22**, 1 (1926)) on urea solutions over the range 40–80°.

⁸ Bencowitz, *J. Phys. Chem.*, **29**, 1432 (1925).

Solutions of Potassium Chloride (Fig. 1).—The data made use of in the preparation of this figure are listed in the following tabular statement with respect to author (with the abbreviated designating letter), temperature range (s denoting the saturated solution), general method of measurement, and reference.

Author	Symbol	Temp. range, °C.	Molality range	Method
Adams ⁹	A	<0	0.005-0.117	Freezing temp.
Berkeley ^{10a}	B	107.4	7.788(s)	Boiling temp.
Berkeley and Appleby ^{10b}	BA	108	7.828(s)	Boiling temp.
Brönsted ¹¹	B'	100	7.535(s)	Boiling temp. (indirect)
Dieterici ¹²	D	0	1.0-3.82	Differential
Edgar and Swan ¹³	ES	19-30	4.56(s)-5.03(s)	Static
Emden ¹⁴	E	14-95	1.35-4.02	Static
Hovorka and Rodebush ¹⁵	H	<0	0.001-0.01	Freezing temp.
Lovelace, Frazer and Sease ⁴ ..	F	20	0.05-4.00	Differential
Nicol ¹⁶	N	70-95	1.11-5.55	Indirect
Pearce and Snow ¹⁷	P	25	0.20-4.81(s)	Dynamic
Rodebush ¹⁸	R	<0	0.95-3.30	Freezing temp.
Sidgwick and Ewbank ^{7a}	SE	5	1.28-3.82	F. p. depression of nitro- benzene
Speranski ¹⁹	S	25-51	4.74-5.82	Differential
Tammann ^{7a}	T	45-100	1.85-3.67	Static
Harrison and Perman ²⁰	P	40-80	0.44-6.90	Static
This paper.....	L	21-44	4.66(s)-5.58(s)	Static

It will be noticed that we have included three sets of measurements of depression of freezing point (δ), this having been done mainly to enable us to continue the curve to zero concentration. These data, for the more dilute solutions, were transformed to our variable by means of the equation²¹ $\log p/p_0 = \log a = -0.004211\delta - 0.00000228\delta^2$, in which a , the relative activity of the water in the solution, is the same as p/p_0 . The foregoing equation is applicable only to solutions so dilute

⁹ Adams, *THIS JOURNAL*, **37**, 481 (1915).

¹⁰ (a) Berkeley, *Trans. Roy. Soc. (London)*, **203A**, 189 (1904). (b) Berkeley and Appleby, *Proc. Roy. Soc. (London)*, **85A**, 489 (1911).

¹¹ Brönsted, *Z. physik. Chem.*, **82**, 621 (1913).

¹² Dieterici, *Ann. Physik*, **42**, 513 (1891).

¹³ Edgar and Swan, *THIS JOURNAL*, **44**, 570 (1922).

¹⁴ Emden, *Ann. Physik*, **31**, 145 (1887).

¹⁵ Hovorka and Rodebush, *THIS JOURNAL*, **47**, 1611 (1925).

¹⁶ Nicol, *Phil. Mag.*, **22**, 502 (1886).

¹⁷ Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

¹⁸ Rodebush, *THIS JOURNAL*, **40**, 1204 (1918).

¹⁹ Speranski, *Z. physik. Chem.*, **70**, 519 (1910).

²⁰ Harrison and Perman, *Trans. Faraday Soc.*, **23**, 1 (1927).

²¹ Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., 1923, p. 284, (a) p. 349.

that the heat of dilution is negligible; otherwise, one must take this factor into account and correct the foregoing results by means of the equation^{21a}

$$\log \frac{a'}{a''} = -\bar{L} \frac{T'' - T'}{2.303RT'T''} + (\bar{C} - \bar{C}_0) \left[\frac{T''(T'' - T')}{2.303RT'T''} - \frac{1}{R} \log \frac{T''}{T'} \right]$$

in which T'' is the temperature chosen for the calculations (in our case 298.1°) and T' is 273.1 - δ ; \bar{L} is the molal heat of dilution at T'' , and \bar{C} and \bar{C}_0 , respectively, the partial molal heat capacity of the solvent in the solution and of the pure solvent; a' is calculated from the simple equation above, and the corrected value a'' is set equal to p/p_0 .

In the application of this equation to the data of Rodebush, the value of \bar{L} was taken from the work of Wüst and Lange,²² and \bar{C} was evaluated from the results of Randall and Bisson²³ by plotting the specific heat of the solution against the concentration in terms of moles of water per mole of salt, and taking the slope of this curve at the several molalities. These values, together with the uncorrected (from a') and corrected values of Δ , are given in Table II.

TABLE II

THE RELATIVE MOLAL VAPOR-PRESSURE LOWERING (Δ) OF SOLUTIONS OF POTASSIUM CHLORIDE, DERIVED FROM THE FREEZING-POINT DATA OF RODEBUSH, CORRECTED FOR THE HEAT OF DILUTION

Moles KCl per 1000 g. H ₂ O M	(Cal. per mole H ₂ O) \bar{L}	\bar{C}	$\frac{p_0 - p}{p_0 M}$	Corr. $\Delta = \frac{p_0 - p}{p_0 M}$
0.0	0.0	17.98
.951	- 2.32	17.96	0.03089	0.03136
1.445	- 5.53	17.93	.03064	.03142
2.331	-13.20	17.86	.03024	.03149
3.043	-19.35	17.77	.03005	.03159
3.192	-20.54	17.75	.03004	.03162
3.300	-21.55	17.74	.02992	.03154

It may be mentioned that we also attempted to derive Δ from the freezing-point data by means of the consideration that the vapor pressure of the solution is the same as that of the ice with which it is in equilibrium. But the values calculated from this basis and the most recent vapor-pressure table²⁴ for ice and water below 0° were not compatible with other data and, indeed, were inconsistent among themselves.

Fig. 1 shows the molal relative vapor-pressure lowering (Δ) caused by potassium chloride in solution as a single curve over the range from extremely dilute to boiling saturated solutions. From 0.3 to 0.8 molal the

²² Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

²³ Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920).

²⁴ Washburn, *Monthly Weather Rev.*, **52**, 488 (1924); based upon a critical examination of all available data.

curve has been dotted as there is some uncertainty on account of the hump in the curve expressing the results of Lovelace, Frazer and Sease alone, which over the rest of the range are clearly the best available; this hump may well be real, for they claim that the irregularity is greater than the possible experimental error, 0.001 in Δ corresponding to 0.0175 in the measured depression. The points listed in Table II lie below the curve, but the difference corresponds to less than 0.05 mm. in p ; this slight discrepancy is probably due to the fact that the heat values used refer to 25° (there being no others available), whereas one should use thermal data which refer to the same temperature as the results to be transformed and corrected.

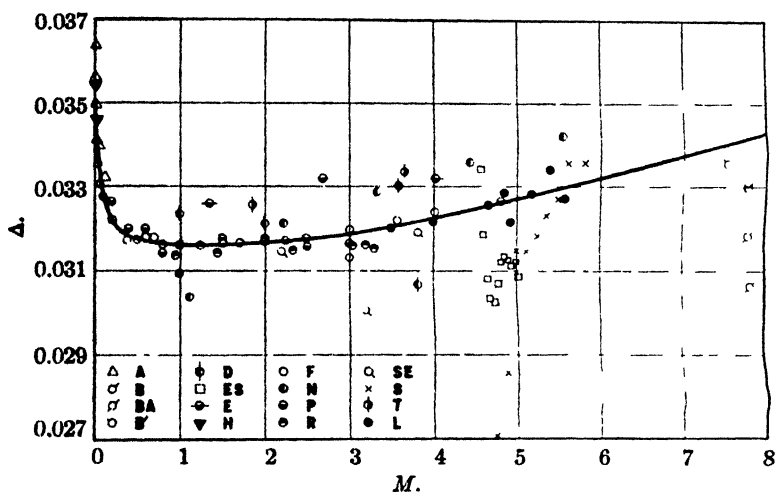


Fig. 1 —The relative molal vapor-pressure lowering of solutions of potassium chloride.

Altogether we venture to believe that this curve gives the best representation of the vapor-pressure data of solutions of potassium chloride now available, it tends to exaggerate the discrepancies, many of the points being off by no more than 0.1 mm. It may be pointed out that the points derived from the measured boiling temperature of the saturated solution all lie considerably below the natural prolongation of the curve—and the same is true for each one of the salts investigated; this corresponds to a somewhat too high vapor pressure or too low surface concentration, and is in line with our repeated observation that the vapor pressure of a saturated solution only attains to its definitive equilibrium value after an interval measured in hours.

Solutions of Sodium Chloride (Fig. 2). The data made use of are listed below, as in the previous case.

Author	Symbol	Δ temperature range, °C.	Molality range	Method
Berkeley ^{10a}	B	107.5	6.760(s)	Boiling temp.
Berkeley and Appleby ^{10b}	BA	108	6.766(s)	Boiling temp.
Bousfield and Bousfield ²⁵	B ²	18	0.56-6.113(s)	Isopiestic solns.
Brönsted ¹¹	B'	100	6.690(s)	Boiling temp.
Dieterici ²⁶	D	0	0.07-0.96	Differential
Emden ¹⁴	E	18-95	0.85-5.13	Static
Harkins and Roberts ²⁷ ...	HR	<0	0.005-0.136	Freezing temp.
Johnston, S. M. ²⁸	J	>100	0.1-2.9	Boiling temp.
Nicol ¹⁶	N	70-95	0.11-0.44	Indirect
Rodebush ¹⁸	R	<0	1.04-5.20	Freezing temp.
Sidgwick and Ewbank ^{7a} ..	SE	5	1.13-5.48	F.-p. depression of nitrobenzene
Smits ²⁹	S'	0	0.04-3.35	Differential
Speranski ^{19,30}	S	24-95	6.14(s)-6.64(s)	Differential
Tammann ^{7a}	T	49-100	2.56-5.13	Static
This paper.....	L	20-50	6.130(s)-6.277(s)	Static

In this case again two sets of freezing data were employed and converted as before into the variable Δ by means of the heat data as determined by Randall and Bisson, and computed by Lewis and Randall.³¹ The uncorrected and corrected values of Δ for the several molalities investigated by Rodebush are:

M	1.045	1.526	2.429	3.057	3.806	4.739	5.201
$\Delta \times 10^6$ (uncorr.)	3181	3212	3279	3339	3432	3535	3596
$\Delta \times 10^5$	3254	3317	3434	3520	3645	3769	3835

These points again lie slightly below our best curve, and probably for the same reason as in the case of potassium chloride.

The experimental work of Bousfield and Bousfield consisted essentially in a comparison of the concentrations of isopiestic solutions of the chlorides of potassium, sodium and lithium. The numerical results, as given by them, are based upon a vapor-pressure curve for sodium chloride solutions (particularly at the lower concentrations) as standard, but this curve is not in satisfactory agreement with the best of the other data cited in Fig. 2 nor do their values for potassium chloride fit the curve in Fig. 1. On the contrary, if their results are recomputed on the basis of the curve (Fig. 1) as standard, the results for sodium chloride lie very close to the curve in Fig. 2, the difference corresponding to only 0.0015 mm. at the

²⁵ Bousfield and Bousfield, *Proc. Roy. Soc. (London)*, **103A**, 429 (1923).

²⁶ Dieterici, *Ann. Physik.*, **67**, 859 (1899).

²⁷ Harkins and Roberts, *THIS JOURNAL*, **38**, 2676 (1916).

²⁸ Johnston, S. M., *Trans. Roy. Soc. (Edinburgh)*, **45**, 855 (1908).

²⁹ Smits, *Z. physik. Chem.*, **51**, 33 (1905).

³⁰ Speranski, *ibid.*, **84**, 160 (1913).

³¹ Ref. 21, p. 350.

lowest concentration and to 0.011 mm. at the highest. Accordingly, this basis was used to evaluate their results for both sodium chloride and for lithium chloride, which also now show excellent agreement with the best curve based on the other data available.

Solutions Saturated with Both Potassium and Sodium Chloride.—In this the method of plotting could not be used, because the molality of these saturated solutions has not been accurately determined.

Solutions of Lithium Chloride (Fig. 3).—Although we did no experimental work on solutions of lithium chloride, it seemed worth while to exhibit its curve for comparison with the other halides. The only data available are those of Lovelace, Bahlke and Frazer³² (F) at 20° for the range 0.097–1.032 *M*, using a differential method; the isopiestic results of

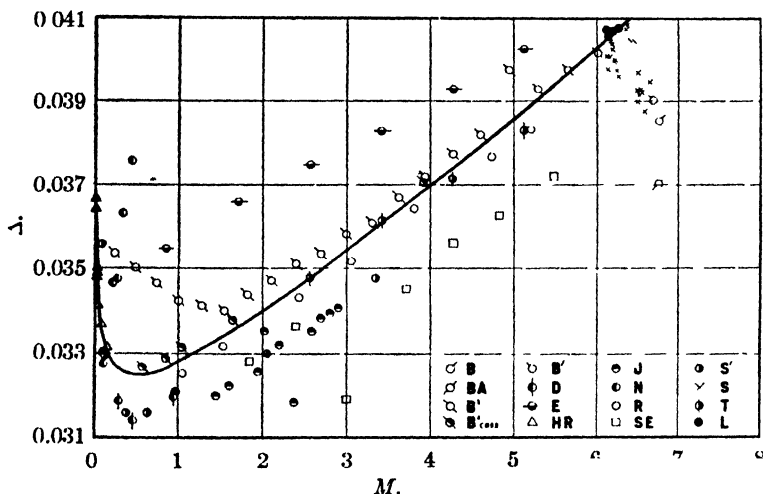


Fig. 2.—The relative molal vapor-pressure lowering of solutions of sodium chloride.

Bousfield and Bousfield (B²) already alluded to; and the freezing-point depression at 0.01 and 0.02 *M* as given by Noyes and Falk³³ (NF). The first-named results are again obviously of a high order of accuracy, and the others are in excellent accord with them.

Comparison of the Curves for the Alkali Halides.—The three curves all start from the same point, Δ for zero concentration of a uni-univalent salt being 0.0355; all three drop sharply to a minimum and then rise again, the most rapid rise corresponding to the minimum at the lowest concentration, and conversely. It is significant that, at concentrations beyond that at which the minimum occurs, the slope is greatest for lithium chloride,

³² Lovelace, Bahlke and Frazer, *THIS JOURNAL*, 45, 2930 (1923).

³³ Noyes and Falk, *ibid.*, 32, 1011 (1910).

which forms a monohydrate stable between 13 and 98°; less for sodium chloride, which appears as hydrate only below 0°; and least for potassium chloride with no known solid hydrates. If hydrates form in solution, the net concentration of the water will be less than its gross concentration, and the observed vapor pressure less than it would otherwise be; this divergence increases with concentration as the relative amount of water

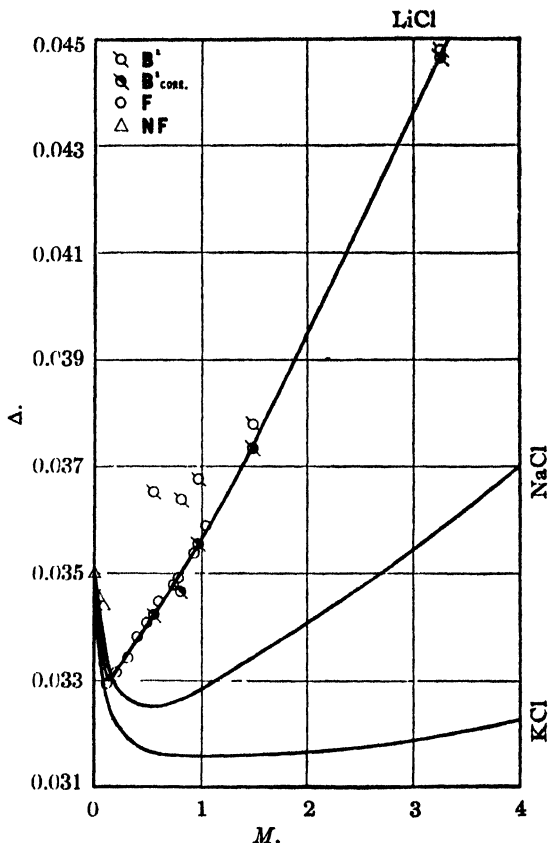


Fig. 3.—The relative molal vapor-pressure lowering of solutions of the chlorides of potassium, sodium and lithium.

decreases. On this basis Δ would, with increasing concentration, increase most rapidly in the case of the salt which we would expect to be hydrated in solution to the greatest extent; this is in harmony with the results for the three halides, and also for the two alkali sulfates.

Sodium Sulfate Solutions (Fig. 4).—The most complete work is that of Wuite³⁴ (W) who made static measurements on solutions saturated

³⁴ Wuite, *Z. physik. Chem.*, **86**, 349 (1914).

with the anhydrous salt at $19.4\text{--}50.4^\circ$ ($3.728\text{--}3.283\text{ }M$) and with the decahydrate at $21.6\text{--}32.4^\circ$ ($1.447\text{--}3.510\text{ }M$), and supplemented these by solubility determinations. There are also data by Tammann^{7a} over the unsaturated range $0.94\text{--}3.44\text{ }M$, and freezing-point data on dilute solutions ($0.025\text{--}0.25\text{ }M$) are given by Noyes and Falk³³ (NF). Some other considerations³⁵ led us to believe that Wuite's value at the transition point is rather low, as indeed we found it to be by 0.9 mm. ; and the measurements at other temperatures indicate that most of Wuite's values are low—this being another illustration of the necessity of maintaining the solution for a period of hours at the temperature before the definitive observation is made. We believe that our points are the more accurate, but have drawn a dotted curve through Wuite's. A few of Tammann's points have been inserted, as well as the values calculated from the freezing data, but no attempt was made to draw a single continuous curve for the decahydrate.

In this case it is obvious that the relative vapor pressure of a solution of constant composition cannot be independent of temperature, for there are two branches of the curve with divergent values of Δ (at different temperatures) for the same molality of solution.

Solutions of Potassium Sulfate and of Potassium Dichromate (Fig. 5).—For potassium sulfate there are data by Berkeley^{10a} and Berkeley and Appleby^{10b} on the boiling temperature (101° , 101.39°) of the saturated solution (1.396 , $1.399\text{ }M$); a similar observation by Brönsted¹¹ (100° , $1.388\text{ }M$); freezing data by Hovorka and Rodebush¹⁵ ($0.001\text{--}0.001\text{ }M$) and from Noyes and Falk³³ ($0.045\text{--}0.25\text{ }M$); together with our own direct measurements.

The curve is similar to that for lithium chloride, though Δ is of course

³⁵ See Norton and Johnston, *Am. J. Sci.*, 12, 467 (1926).

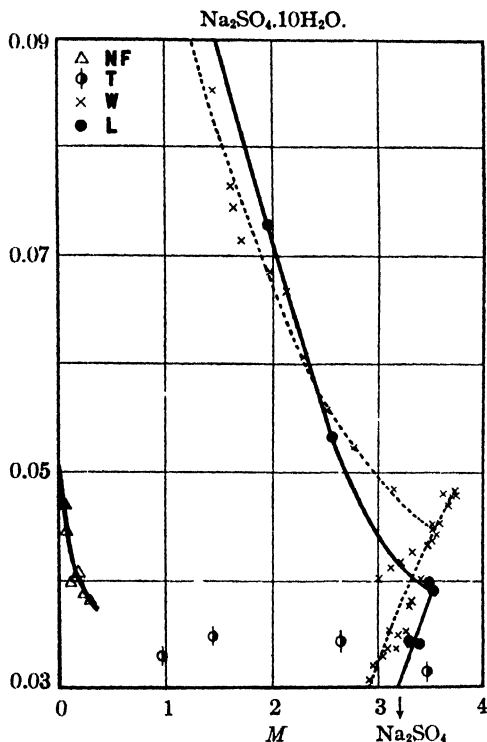


Fig. 4.—The relative molal vapor-pressure lowering of solutions of sodium sulfate.

higher, being above 0.055 at zero concentration. It will be observed that the boiling data again lie considerably below the probable course of the curve.

For potassium dichromate there are no data except ours; in this case the curve appears to have a negative slope over the range investigated. This implies that the complete curve from zero concentration would first fall, then rise and then fall again; but the data are insufficient to decide this question; this course, it may be remarked, would in effect be similar to that of the curve for potassium chloride if the "hump" is real.

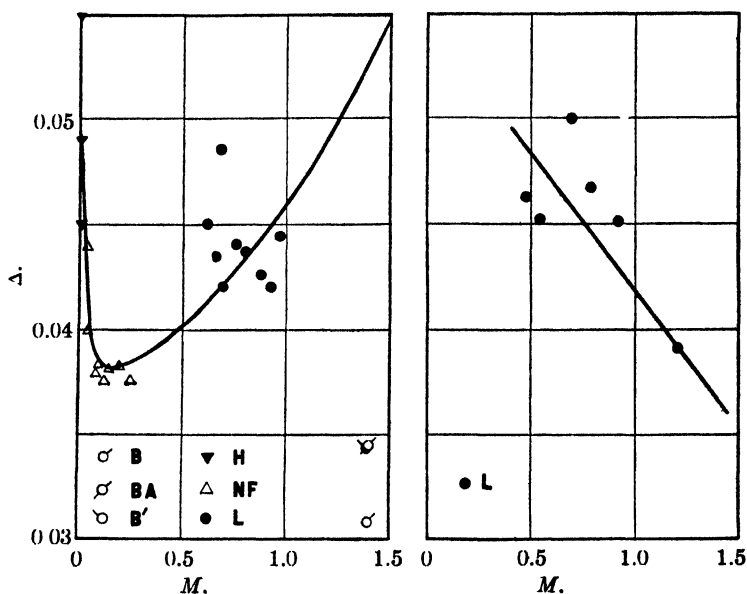


Fig 5.—The relative molal vapor-pressure lowering of solutions of potassium sulfate (left) and potassium dichromate (right).

Conclusion

From the curves for the several salts, plotted on a large scale, values at a series of concentrations were read off; they are presented in Table III. Similarly we have derived, and give in Table IV, values of the percentage humidity in equilibrium with saturated solutions of the several salts at a series of temperatures, and believe that these are more reliable than those hitherto available for these salts. We have also made use of the data to plot the molality of the solutions against that of the isopiestic solution of potassium chloride; from the curves, which are of gentle curvature (though they cannot be represented over the whole range by a single quadratic equation) we have read off the results listed in Table V for four of the salts,

TABLE III

INTERPOLATED VALUES OF THE RELATIVE MOLAL VAPOR-PRESSURE LOWERING (Δ) FOR THE SEVERAL SALTS

<i>M</i>	KCl	NaCl	LiCl	Na ₂ SO ₄ ^a	Na ₂ SO ₄ ·10H ₂ O	K ₂ SO ₄	K ₂ Cr ₂ O ₇
0.01	0.03444	0.03500	0.03500	0.0481	0.0476
.02	.03416	.03464	.03468	.04680447
.04	.03364	.03420	.03420	.04500415
.08	.03296	.03355	.03326	.04280388
.10	.03277	.03338	.03305	.03900385
.2	.03220	.03285	.033210383
.4	.03182	.03253	.033780394	0.0498
.5	.03175	.03250	.034070402	.0485
.6	.03169	.03252	.034370411	.0472
.8	.03162	.03264	.035000434	.0445
1.0	.03160	.03283	.035670460	.0419
1.5	.03161	.03340	.03744	0.0895	.0548
2.0	.03169	.03404	.039400711
2.5	.03178	.03472	.041450547
3.0	.03192	.03545	.04355	0.0251	.0443
3.5	.03209	.03620	.04568	.0386	.0389
4.0	.03228	.03699
4.5	.03251	.03778
5.0	.03275	.03860
5.5	.03300	.03945
6.0	.03323	.04031
6.5	.03348	.04118
7.0	.03372
7.5	.03396
8.0	.03421

^a At 32.38° (tr. point) $M = 3.512$; $p = 31.47$ mm.; $(p_0 - p)/p_0 M = 0.03885$.

TABLE IV

THE ACTIVITY OF WATER AT REGULAR INTERVALS OF TEMPERATURE IN SOLUTIONS SATURATED WITH THE SEVERAL SALTS

Temp., °C.	KCl		NaCl		Na ₂ SO ₄		K ₂ SO ₄		K ₂ Cr ₂ O ₇	
	<i>M</i>	100 <i>p/p</i> ₀	<i>M</i>	100 <i>p/p</i> ₀	<i>M</i>	100 <i>p/p</i> ₀	<i>M</i>	100 <i>p/p</i> ₀	<i>M</i>	100 <i>p/p</i> ₀
10	4 150	86.58	6 103	75.29	0 526	97.88
20	4 603	85.01	6 128	75.16	638	97.35	0 418	97.93
30	5 029	83.53	6 168	74.96	744	96.82	.628	97.06
40	5 428	82.11	6 217	74.70	3 409	87.61	.847	96.28	.897	96.12
50	5 682	81.20	6 276	74.41	3 290	89.14	.949	95.70	1 201	95.28
60	6 117	79.64	6 344	74.05	3 180	90.43	1 044	95.14
70	6 476	78.33	6 420	73.65	3 089	91.47	1 138	94.53

TABLE V

MOLALITIES OF ISOPIESTIC SOLUTIONS

KCl	NaCl	LiCl	K ₂ SO ₄
0.010	0.010	0.010	0.008
.020	.020	.020	.018
.040	.040	.040	.036
.080	.080	.080	.070
.100	.098	.098	.088

TABLE V (Concluded)

KCl	NaCl	LiCl	K ₂ SO ₄
.2	.197	.188	.172
.4	.393	.373	.328
.5	.488	.465	.403
.6	.580	.558	.476
.8	.772	.724	.610
1.0	.964	.890	.736
1.5	1.425	1.284	1.020
2.0	1.873	1.660	1.247
2.5	2.303	2.011	1.464
3.0	2.730	2.343	
3.5	3.145	2.665	
4.0	3.559	2.976	
4.5	3.960	3.273	
5.0	4.367	3.562	
5.5	4.756	...	
6.0	5.139	...	
6.5	5.514	...	
7.0	5.888	...	
7.5	6.260	...	
8.0	6.608	...	

Summary

The vapor pressure of the solution saturated with potassium chloride, sodium chloride, potassium sulfate, sodium sulfate, potassium dichromate, and with both potassium chloride and sodium chloride has been measured by a static method, with an accuracy of about 0.05 mm., over the temperature range 20 to 50°. Each solution was kept at constant temperature for at least 24 hours before the definitive reading was made; inattention to this necessary precaution by most previous authors has resulted in values which are slightly in error, as if the concentration of the solution at its surface was not precisely the saturation concentration. The various data for solutions of each salt up to saturation have been correlated by a sensitive method of plotting; the resulting curves are a more reliable picture of the vapor pressure of these solutions than has hitherto been available.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE FREE ENERGY OF AURIC OXIDE AS DETERMINED FROM MEASUREMENTS OF THE GOLD-AURIC OXIDE ELECTRODE¹

BY T. F. BUEHRER AND W. E. ROSEVEARE

RECEIVED JULY 1, 1927

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The purpose of this investigation was to measure the potential of the gold-auric oxide electrode and to calculate the free energy of formation of auric oxide from its elements at 298° A.

The cell chosen for these measurements was H_2 (g), H_2SO_4 (x-M), Au_2O_3 (s), Au (s). A careful search of the literature showed that very little work had been done on the potential of the gold-auric oxide electrode. Jirsa and Jelinek² in their work on the anodic oxidation of gold arrived at a value of 1.36 volts, referred to hydrogen. The aim of the present research was to extend the accuracy of this value, if possible, by the use of cell substances of such purity and homogeneity that true equilibrium would readily be established within the cells.

Materials and Apparatus

The measurements were made with auric oxide obtained by precipitation from chloro-auric acid by means of potassium hydroxide, followed by a purification process as described in a previous paper by the authors.³ The gold was obtained in excellent crystalline form by reduction of chloro-auric acid with ferrous sulfate. The cells were of the type devised by Lewis and Rupert,⁴ modified to contain two hydrogen electrodes and three gold half-cells, to make possible a triplicate series of measurements under identical conditions. Three concentrations of sulfuric acid were employed: 1.024 *M*, 0.100 *M* and 0.0100 *M*. The auric oxide as well as the gold crystals were equilibrated with the sulfuric acid solutions for 12 hours before being introduced into the cells. Hydrogen from the electrolysis of potassium hydroxide was used in the cells. All electromotive-force measurements were made with a Type K Leeds and Northrup potentiometer. The water-bath containing the cells was maintained at $25^\circ \pm 0.1^\circ$. The cells came to equilibrium promptly in most cases, the more so when the more concentrated solutions of sulfuric acid were used. The measurements are summarized in Table I.

The electromotive force is seen to be substantially independent of the concentration of the sulfuric acid, as is to be expected from the cell reaction.

¹ Abstract of a thesis submitted by William Earl Roseveare in partial fulfilment of the requirements for the Degree of Master of Science in the University of Arizona, June, 1926.

² Jirsa and Jelinek, *Z. Elektrochem.*, **30**, 286 (1914); *ibid.*, 534 (1924); *Chem. Listy*, **18**, 1 (1924).

³ Roseveare with Buehrer, *THIS JOURNAL*, **49**, 1221 (1927).

⁴ Lewis and Rupert, *ibid.*, **33**, 229 (1911).

TABLE I

DIRECT MEASUREMENTS OF POTENTIAL OF THE GOLD-AURIC OXIDE ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT 25°

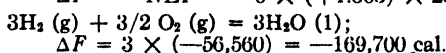
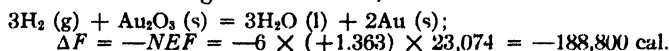
Concn H ₂ SO ₄	Cell 1	Cell 2	E.m.f. (volts)	Cell 3	Mean
1.024	1.363 ₄	1.363 ₄		...	1.363 ₄
0.1000	1.362 ₇	1.363 ₀		1.364 ₉	1.363 ₈
.0100	1.363 ₈	1.364 ₂		1.363 ₇	1.363 ₉

General average = 1.364 ± 0.001 volts

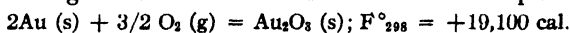
These results have recently been confirmed independently by Gerke and Rourke, in an investigation⁵ in which they measured the potential of the cell Hg(l), Hg₂SO₄(s), H₂SO₄(x-M), Au₂O₃(s), Au(s) and from the known value of the potential cell H₂(g), H₂SO₄(x-M), Hg₂SO₄(s), Hg(l) calculated the electromotive force of the gold-auric oxide electrode against the hydrogen electrode. Their calculated mean value was 1.362 ± 0.002 volts.

The Free Energy of Auric Oxide

To obtain the free energy of auric oxide from these measurements, it is necessary to combine the free energy of the reaction tending to take place in the above cell with the free energy of formation of 1 mole of liquid water from its elements at 298° Å., which was calculated by Lewis and Randall⁶ to be -56,560 calories. We shall use the value of the e.m.f. of the gold-auric oxide electrode Au, Au₂O₃, H⁺, E° = -1.363 ± 0.001 volts, which is the average of our result, and that of Gerke and Rourke.



Subtracting the first from the second of these equations, we obtain:



This high positive free energy of formation of auric oxide indicates that it must be very unstable and, therefore, have a high dissociation pressure. The auric oxide involved in the above equation is very probably not Au₂O₃, but a hydrated form of the oxide. Because of its instability, it is a question whether the true degree of hydration of auric oxide can be experimentally determined.

The Dissociation Pressure of Auric Oxide

The dissociation pressure of auric oxide as calculated by the thermodynamic equation $\Delta F = -RT \ln K$ is found at 298° Å. to be 2.13×10^9 atmospheres.

It was also considered of interest to calculate the entropy change attending the formation of 1 mole of auric oxide from its elements at 298° Å.

⁵ Gerke and Rourke, THIS JOURNAL, 49, 1855 (1927).

⁶ Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., 1923, p. 485.

According to Thomsen⁷ the value of ΔH for this reaction is $-13,200$ cal. for $1 \text{ Au}_2\text{O}_3 (\text{Aq.})$ whence $\Delta S_{298} = (\Delta H - \Delta F)/T = (-13,200 - 19,100)/-298 = -108.4$ cal./mol./degree.

The writers wish to express their appreciation to Professor G. N. Lewis, who suggested this investigation.

Summary

1. Measurements have been made on the cell: $\text{H}_2(\text{g})$, $\text{H}_2\text{SO}_4(\text{x-M})$, $\text{Au}_2\text{O}_3(\text{s})$, $\text{Au}(\text{s})$, at three concentrations of sulfuric acid and at 25° . The electromotive force is seen to be substantially independent of concentration of sulfuric acid, the general average value being 1.364 ± 0.001 volts.

2. The free energy of formation of auric oxide from its elements, its dissociation pressure, and entropy of formation at 298°A. are calculated, all of which indicate that auric oxide is a very unstable compound.

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NOTES

Confirmatory Test for Aluminum.—The test suggested is a modification of that proposed by Attack.¹ It has the advantage that the reagent need not be freshly prepared each time. Further, the color absorption is greater.

The reagent consists of a saturated solution of alizarin in concd. acetic acid.

After separating the aluminum hydroxide from any chromium and zinc, it is washed, dissolved in hydrochloric acid and then reprecipitated with a slight excess of ammonium hydroxide. To this solution is added one drop of the alizarin reagent which imparts an apple-blossom pink coloration to the aluminum hydroxide. The latter will soon settle out, leaving the solution above colorless.

CONTRIBUTION FROM THE
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Plastic Films and the Drop-Weight Method of Interfacial Tension Measurement.—The drop-weight method of measuring surface and interfacial tensions has in recent years been greatly refined by Harkins and his co-workers.¹ Not only have they improved the apparatus in a

⁷ Thomsen, "Thermochemistry," Longmans, 1908, p. 201.

¹ Attack, *Chem. Zentr.*, [1] 82, 176 (1916).

¹ Harkins and Brown, *THIS JOURNAL*, 41, 499 (1919).

mechanical sense but they have also shown that the law of Tate does not apply strictly, since the shape of the drop has an important effect upon the size of each drop, and therefore upon the number of drops formed from a given volume of liquid. It has been found that for reversible conditions a satisfactory correction for the shape effect can be made if the radius of the tip and the size of the drop formed are known.

In view of the importance of the shape development of the drops it is interesting to consider the possible effects of plastic film formation.

The work of Wilson and his students² is illuminating in regard to the thickness and mechanical properties of such films. They have determined that the surface films (solid or jelly?) formed by sodium stearate on its aqueous dispersions may attain a thickness of 10 to 40 microns³ and that such films exhibit frictional or plastic characteristics.⁴ They also very cleverly demonstrated that a solution of saponin (1 to 1000) with Nujol or castor oil gives an interfacial film exhibiting distinct frictional qualities.⁵ Holmes⁶ also discusses the mechanism of the building up of thick solid films and describes a very thick film formed between water and a benzene dispersion of gum dammar. Bancroft⁷ states that by adding salt to a soap solution the soap film can be made to come out so brittle that it will not form a satisfactory emulsion of oil in water. He believes that for good emulsification the film formed must be tough and elastic.

The above references are sufficient to show that one must consider the possibility of interfacial films being thick and either plastic and tough, or brittle. Plasticity, of course, connotes resistance to flow under low shear.

It has been commonly assumed that plastic films, if developed during the formation of a drop suspended from a dropping tip, would increase the drop size and the apparent interfacial tension. This assumption has as its corollary that plastic films can never be the cause of low apparent interfacial tensions. Is such an assumption justified? I believe not.

If a plastic film is formed around a partially developed drop the effect will be the same as though one had slipped a perfectly fitting casing of plastic material over the drop. If further solution tries to enter such an encased drop this plastic solid casing will resist distention and in order that the drop may increase its volume the body of the drop will be forced away from the dropping tip, thus tending to form an elongated drop.

² Wilson and Ries, "First Colloid Symposium Monograph," J. H. Mathews, University of Wisconsin, Madison, Wisconsin, 1923, p. 145.

³ Ref. 2, p. 164.

⁴ Ref. 2, pp. 154-161.

⁵ Ref. 2, p. 167, Fig. 18.

⁶ Holmes, "Colloidal Behavior" (Bogue), McGraw-Hill Book Co., New York, 1924, pp. 222-232.

⁷ Bancroft, "Applied Colloid Chemistry," McGraw-Hill, New York, 1926, p. 352.

Since this elongated drop is formed as the result of a mechanical constriction and the increased surface is not in harmony with the volume of the drop and the interfacial tension, the chances for the drop to snap off before reaching full development are very good.

In extreme cases, that is, in cases in which the interfacial film is both rapidly formed and very tough, the elongated drop shape will be stabilized, as in the case of the drop shown in Wilson's Fig. 18. Another complication which may well arise is the actual adhesion of such a film to the dropping tip. Harkins seems to have had this in mind in referring to a determination⁸ in which he obtained an "interfacial tension" of 0.04 dyne/cm. by dropping water containing 0.1 *M* sodium hydroxide and sodium chloride into benzene containing 0.1 *M* oleic acid. He states (p. 77) "In this case a solid film forms, and this causes the drops to hang longer than usual, but the minute value of the tension indicates that the tensile strength of the film is very low." As pointed out above, the "minute value" of the "interfacial tension" may mean that the film is strong and prevents the development of the drop. McBain and Burnett⁹ emphasize the tendency for the formation of solid soap curds when salt is present in a soap solution; it is likely that solid films were formed in the case of other determinations reported in Harkins' paper. It would be interesting to know the magnitude of the deviation of individual determinations from the reported mean in the case of certain of these determinations. The check data given on p. 79 are either misprinted or reveal a deviation of 50% among check determinations.

To return to the non-equilibrium "interfacial tension" which Harkins reports as 0.04 dyne/cm. it is worth while to consider, first, the conditions at this "interface" and, second, the definition of interfacial tension. Starting from the inside of the drop we have (1) aqueous solution, (2) interface between aqueous solution and solid soap phase, (3) solid soap phase, (4) interface between solid soap phase and benzene dispersion of fatty acid. *If the solid soap phase touches the dropping tip, there will be no liquid liquid-interface.* The soap film is solid; it will resist distention and will crinkle if the drop tends to grow smaller.

If the soap film does not touch the tip, there will be a true liquid liquid-interface next the tip, but not elsewhere.

Interfacial tension as defined by Willows and Hatschek¹⁰ involves only reversible forces, the stress per cm. being independent of the size of the surface. Clearly, if a plastic solid film touches the dropping tip and completely surrounds the drop there can be no interfacial tension.

⁸ Harkins and Zollman, *THIS JOURNAL*, **48**, 69 (1926).

⁹ McBain and Burnett, *J. Chem. Soc.*, **121**, 1332 (1922).

¹⁰ Willows and Hatschek, "Surface Tension and Surface Energy," P. Blakiston's Son and Co., Philadelphia, 1923, p. 2.

Measurements made under conditions which make it probable that such a condition existed during the determinations should not be reported as "interfacial tensions," because they can in no way satisfy the fundamental requirement of reversibility.

In case the plastic film merely approaches but does not touch the tip, a true liquid liquid-interface will exist next the tip and the plastic film can only affect the results by influencing the shape development of the drop. Since the correction factor, which is dependent upon the shape development, varies from 1.3 to 1.8, it seems conservative to state that it is impossible to ignore any condition or set of conditions which is capable of affecting this shape development.

STEWART S. KURTZ, JR.

RECEIVED JUNE 6, 1927
PUBLISHED AUGUST 5, 1927

The Purification of Toluene for Thermo-Regulators.—For use in a mercury-toluene thermo-regulator the toluene must be free from traces of certain impurities, notably sulfur compounds, which will foul the surface of the mercury and interfere with the sharp adjustment of the regulator. According to Vanino,¹ toluene may be purified by washing it repeatedly with sulfuric acid, then with water until the washings are neutral to litmus paper, and finally drying the toluene over metallic sodium.

A quantity of c. p. toluene purified according to Vanino's directions was still found to corrode the mercury. It occurred to us to determine the effect of sodium amalgam. The toluene was accordingly boiled under a reflux condenser with sodium amalgam containing 1% of sodium. The toluene was then decanted, washed with water and finally distilled. The water remaining in the toluene was all removed with the first small fraction of the distillate, which was accordingly rejected.

The toluene purified in this manner has been in use for several months without showing any action upon the surface of the mercury.

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B. L. SOUTHER

RECEIVED JUNE 9, 1927
PUBLISHED AUGUST 5, 1927

¹ Vanino, "Handbuch der präparativen Chemie," Organischer Teil, p. 345.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

METALLIC SALTS OF LOPHINE, 1,2,4-TRIAZOLE AND TETRAZOLE

BY HAROLD H. STRAIN

RECEIVED JANUARY 27, 1927

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Introduction

When negative groups are substituted for one or two hydrogen atoms of a molecule of ammonia, a compound is obtained which is related to ammonia as the familiar oxygen acids are related to water. Such ammonia derivatives must therefore be regarded as acids of an ammonia system of compounds,¹ and in order to distinguish them from the oxygen or aquo acids, Franklin has called them ammono acids. A number of these ammono acids are known; for example, hydrocyanic acid or ammono carbonous acid, cyanamide or ammono carbonic acid, benzamidine or ammono benzoic acid, etc.

In general, the ammono acids are much weaker than the corresponding aquo acids, as shown by the inability of many of them to form metallic salts in the presence of water. However, by carrying out reactions in liquid ammonia, a poorer solvolytic solvent than water, Franklin² has shown that it is possible to prepare metallic salts of the very weak ammono acids pyrrole, indole and carbazole.

The ammono acids just mentioned owe their acid properties to the negative influence of the doubly bonded carbon atoms. Now, since nitrogen is a more electronegative element than carbon, it seems reasonable to expect that the acid properties of a compound such as pyrrole would be accentuated by substituting a nitrogen atom for a CH-member of the ring, while further substitution by nitrogen atoms would produce still stronger acids. Accordingly, pyrrole,

imidazole, $\begin{array}{c} \text{CH}=\text{CH} \\ | \qquad \qquad \qquad \diagup \\ \text{CH}=\text{CH} \end{array} \text{NH}$; 1,2,4 triazole, $\begin{array}{c} \text{CH}=\text{N} \\ | \qquad \qquad \qquad \diagup \\ \text{N}=\text{CH} \end{array} \text{NH}$; and tetrazole, $\begin{array}{c} \text{CH}-\text{N} \\ | \qquad \qquad \qquad \diagup \\ \text{N}=\text{N} \end{array} \text{NH}$ should be am-

mono acids, their strength increasing in the order given. Furthermore, alkyl and aryl derivatives of the above compounds should be acids, providing one hydrogen atom remains attached to a nitrogen atom, the strength of the resulting acid being dependent upon the negative character of the substituted group. Thus, lophine, triphenylimidazole,

$\begin{array}{c} \text{C}_6\text{H}_5\text{C}-\text{N} \\ || \qquad \diagup \\ \text{C}_6\text{H}_5\text{C}-\text{NH} \end{array} \text{CC}_6\text{H}_5$, should be a stronger acid than imidazole.

¹ Franklin and Stafford (a) *Am. Chem. J.*, **28**, 83 (1902); (b) Franklin, *Eighth Int. Cong. App. Chem.*, **6**, 119 (1912); (c) *THIS JOURNAL*, **37**, 2279 (1915); (d) **46**, 2137 (1924).

² Franklin, *J. Phys. Chem.*, **24**, 81 (1920).

Since, formally at least, the nitrogen compounds just mentioned are ammonio acids, they should react with the more electropositive elements and their amides to form salts^{1a,c} if the reactions be carried out in a poor solvolytic solvent such as ammonia. These compounds should also show conductivities characteristic of weak acids when dissolved in liquid ammonia.

The following experiments show that imidazole, lophine, triazole and tetrazole react with sodium, calcium and magnesium and with the amides of lithium, sodium, potassium, copper and silver, forming salts, while conductivity measurements indicate that the strength of the acid is dependent upon the negative character of the components of the molecule.

Unless otherwise stated, all salts were prepared in liquid ammonia solution. The methods of manipulation, such as handling the liquid ammonia, drying the salts, determining the ammonia of crystallization and preparing the salts for analysis, were essentially the same as those previously described by Franklin.³ All the salts thus prepared were unstable in the presence of water, being hydrolyzed to the acid and to the metallic hydroxide.

Metallic Salts of Imidazole

Imidazole dissolves abundantly in liquid ammonia, forming a clear solution from which the imidazole may be obtained by evaporation of the solvent, there being no formation of an ammonium salt. Wenzel,⁴ working in this Laboratory, found that imidazole in ammonia solution attacks magnesium slowly, setting hydrogen free and forming a slightly soluble magnesium salt. Wenzel has also prepared the potassium, sodium, calcium and silver salts of imidazole. However, Wyss⁵ had previously prepared the silver salt.

Metallic Salts of Lophine

Lophine, prepared by heating hydrobenzamide,⁶ is only slightly soluble in liquid ammonia at room temperature, while at -35° it is practically insoluble. Lophine does not form an ammonium salt.

Metallic Salts of 1,2,4-Triazole

Preparation of Triazole.—According to Pellizzari,⁷ two molecules of formamide distilled with one molecule of hydrazine hydrochloride form 1,2,4-triazole in poor yields. Substitution of hydrazine sulfate for hydrazine hydrochloride did not increase the yields. It was found, however, that a yield amounting to one-sixth of the theoretical could be

³ Franklin, *J. Phys. Chem.*, **15**, 513 (1911).

⁴ Wenzel, unpublished work.

⁵ Wyss, *Ber.*, **10**, 1373 (1877).

⁶ Radziszewski, *Ber.*, **10**, 70 (1877).

⁷ Pellizzari, *Gazz. chim. ital.*, **4**, II, 222 (1894), *Ber.*, **27**(R), 801 (1894).

TABLE I
SALTS OF LOPHINE^a

Metal	Formula	Cryst. form	Color	Solubility	M. calcd.	M. found	N calcd.	N found	Moles of NH ₃ of cryst.
Mg ^b	Mg(C ₂₁ H ₁₈ N ₂) ₂	...	colorless	sl. sol.	3.96	3.4	9.3
Ca ^c	Ca(C ₂₁ H ₁₈ N ₂) ₂ ·6NH ₃ and Ca(C ₂₁ H ₁₈ N ₂) ₂	Long prisms with pointed ends white powder	colorless	m. sol.	6.4	6.5 6.2	8.9	10.7 9.4	6.0 6.7
K ^d	KC ₂₁ H ₁₈ N ₂ ·3NH ₃ KC ₂₁ H ₁₈ N ₂	...	colorless	v. sol.	11.7	11.6 11.3 11.2	8.4
Ag ^e	AgC ₂₁ H ₁₈ N ₂ ·2NH ₃ AgC ₁₅ H ₁₄ N ₂	small prisms powder	colorless gray	sl. sol.	26.8	27.4	7.0	7.0	...
Cu ^{+ + f}	Cu(C ₂₁ H ₁₈ N ₂) ₂ ·XNH ₃	large cubes or plates	greenish-blue	sl. sol.	9.7	9.5	8.6	8.5	6.2
Cu ^{+g}	Cu(C ₂₁ H ₁₈ N ₂) ₂ CuC ₂₁ H ₁₈ N ₂	powder small prisms	9.6	...	8.2	7.5
Li ^h	LiC ₂₁ H ₁₈ N ₂ ·XNH ₃ LiC ₂₁ H ₁₈ N ₂	large prisms prisms	orange colorless	sol. sol.	2.3	2.0	not determined
Na ⁱ	NaC ₂₁ H ₁₈ N ₂	Not crystallized	...	v. sol.	7.2	8.7

^a The abbreviations used in this table are: M., metal; N, nitrogen; sol., soluble; sl., slightly; m., moderately; v., very. The percentage compositions of these compounds are all based on the anammonous (dry) salts.

^b Magnesium and calcium lophine react with liquid ammonia, forming ammonio basic salts as indicated by the high nitrogen analyses. If a reducing agent is present, these salts form highly red-colored solutions.

^c The calcium salt was prepared by the action of lophine on a solution of metallic calcium in liquid ammonia and by the action of lophine on calcium amide.

^d Prepared by the action of lophine on potassium amide.

^e Prepared by the action of lophine on silver amide and by the action of potassium lophine on silver nitrate.

^f Prepared by treating a solution of cupric nitrate with potassium lophine. The vapor pressure of the ammonated salt did not reach a constant value, hence the ammonia of crystallization could not be accurately determined.

^g Prepared by treating cuprous amide with lophine.

^h Prepared by the action of lophine on lithium amide.

ⁱ Prepared by the action of lophine on sodium amide.

obtained by adding two molecules of finely divided potassium hydroxide to the above mixture and allowing it to dissolve completely before distilling.

The distillation was made in a Pyrex flask over a luminous flame, while the distillate was collected in a balloon flask cooled in an ice-and-salt mixture. The semi-solid condensate was extracted with boiling ethyl acetate from which the triazole separated upon cooling. The crystals, after recrystallization from alcohol, melted at 120–121°.

Triazole is very soluble in liquid ammonia, forming a clear solution. Upon evaporation of the solvent, crystals of triazole are obtained, thus showing that triazole does not form an ammonium salt.

Until the following preparations were made, cupric triazole was the only metallic salt of triazole known. It was prepared by Pellizzari and Cuneo⁸ as a blue precipitate when triazole was added to a neutral or slightly alkaline aqueous solution of a copper salt.

TABLE II
SALTS OF 1,2,4-TRIAZOLE^a

Metal	Formula	Cryst. form	Color	Solubility	M. calcd.	M. found	Moles of NH ₃ of crystallization
Na ^b	NaC ₂ H ₂ N ₃	...	colorless	v. sol.	25.3	26.4	Not determined
Ag ^c	AgC ₂ H ₂ N ₃ ·NH ₃	tetrahedra	colorless	m. sol.	61.4	60.8	1.0
	AgC ₂ H ₂ N ₃	powder	gray			61.8	...
Mg ^d	Mg(C ₂ H ₂ N ₃) ₂ ·4NH ₃	small prisms	white	sl. sol.	15.1	13.5	4.3
	Mg(C ₂ H ₂ N ₃) ₂					12.8	3.7
						15.0	4.1
Ca ^e	Ca(C ₂ H ₂ N ₃) ₂ ·XNH ₃	small prisms	white	sl. sol.	22.8	22.6	Not determined
Cu ^f	Ca(C ₂ H ₂ N ₃) ₂	finely cryst.	white	sl. sol.	48.3	50.4	Not determined
	CuC ₂ H ₂ N ₃ ·XNH ₄						
	CuC ₂ H ₂ N ₃						

^a Since the salts were removed from the reaction tubes in aqueous solution, the Kjeldahl method for the determination of nitrogen was the only one which was applicable. However, it was found that unchanged triazole escapes with the vapors of the acid; hence, no nitrogen determinations were made. The analytical results are based on the anammonous salts.

^b Prepared by the action of triazole on sodium amide.

^c Prepared by the action of triazole on silver amide.

^d Prepared by the action of triazole on magnesium.

^e Prepared by treating a solution of calcium in liquid ammonia with triazole.

^f Prepared by the action of triazole on cuprous amide.

Metallic Salts of Tetrazole

The tetrazole used in the following preparations was made from its carboxylic acid which was prepared according to the method of Oliveri-Mandalá and Passalacqua.⁹ After the tetrazole had been recrystallized thrice it was deemed sufficiently pure.

Tetrazole is sufficiently acidic so that many of its salts have been pre-

⁸ Pellizzari and Cuneo, *Ber.*, **27**(R), 407 (1894).

⁹ Oliveri-Mandalá and Passalacqua, *Gazz. chim. ital.*, **41** (II), 430 (1911).

pared in aqueous solution. Thiele and Ingle¹⁰ have reported the sodium and barium salts, Bladin¹¹ has prepared the silver and copper salts, while Bauer¹² has measured the electrical conductivity of aqueous solutions of free tetrazole.

Ammonium Tetrazole, NH_4CHN_4 .—Tetrazole reacts with gaseous ammonia, forming the ammonium salt which is fairly soluble in liquid ammonia. This salt was analyzed by distilling the ammonia from a dilute aqueous solution made alkaline with sodium hydroxide.

Anal. Calcd. for NH_4CHN_4 : NH_3 , 19.8. Found: 19.5.

Calcium Tetrazole, $\text{Ca}(\text{CHN}_4)_2$.—Tetrazole was allowed to react with metallic calcium in liquid ammonia solution. The blue color due to the calcium was rapidly dispelled, a quantity of hydrogen almost equivalent to the amount of metal used was rapidly evolved, while long, needle-like crystals were obtained by concentrating the solution.

A second preparation of this salt was made by treating calcium amide with tetrazole, the calcium being determined as oxalate.

Anal. Calcd. for $\text{Ca}(\text{CHN}_4)_2$: Ca, 22.2. Found: Ca, 21.8.

Conductivity Measurements

The electrical conductances of ammonia solutions of pyrrole, imidazole, triazole and tetrazole¹³ were measured in an apparatus similar to that described by Elsey.¹⁴ Lophine is so insoluble in ammonia that a sufficiently concentrated solution could not be obtained for accurate measurements.

In Table III the dilution is given in liters per mole. The values of the equivalent conductivity in Kohlrausch units were obtained by interpolation of the curves plotted from the conductivity measurements.

TABLE III
EQUIVALENT CONDUCTIVITIES OF SOLUTIONS OF PYRROLE, IMIDAZOLE, TRIAZOLE AND
TETRAZOLE IN LIQUID AMMONIA

Dilution $\Phi \times 10^{-3}$	8	16	32	64	128	256	512	1024	2048	4096	8192
Pyr- role A	0.034	0.044	0.070
Imida- zole A	...	0.59	0.70	0.90	1.10	1.40
Triazole A	60	75	91	115	142	169	197	225	245
Tetra- zole A	128	151	174	197	217	236	249	259

¹⁰ Thiele and Ingle, *Ann.*, **287**, 247 (1895).

¹¹ Bladin, *Ber.*, **25**, 1413 (1892).

¹² Bauer, *Ann.*, **287**, 249 (1895).

¹³ The pyrrole used in measuring the conductivity was purified according to the method of Ciamician and Dennstedt [*Ber.*, **19**, 173 (1886)]. The imidazole, which was contributed by Wenzel and which he had purified by distillation, was recrystallized from toluene. The triazole and tetrazole were obtained sufficiently pure by recrystallizing portions of the specimens used in preparing the metallic salts.

¹⁴ Elsey, *THIS JOURNAL*, **42**, 2454 (1920).

The author wishes to take this opportunity to express his sincere thanks to Dr. E. C. Franklin, at whose suggestion and under whose careful and kindly direction this investigation was carried out.

Summary

Any compound which is derived from ammonia by substituting negative groups for one or two of the three hydrogen atoms is an ammono acid.

The strength of the ammono acids is dependent upon the negative character of the components of the molecule; thus, the acidity of pyrrole, imidazole, triazole and tetrazole increases in the order given as shown by the conductivity measurements.

A number of the metallic salts of the ammono acids lophine, triazole and tetrazole have been prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,
No. 550]

ESTABLISHMENT OF THE OPTIMAL HYDROGEN-ION ACTIVITIES FOR THE ENZYMIC HYDROLYSIS OF STARCH BY PANCREATIC AND MALT AMYLASES UNDER VARIED CONDITIONS OF TIME AND TEMPERATURE¹

BY H. C. SHERMAN, M. L. CALDWELL AND MILDRED ADAMS

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The development of our investigation of the amylases and related enzymes makes it important now to know, and to be able experimentally to establish and maintain, the reaction most favorable to the activity of each enzyme under investigation throughout a wider range of time and temperature than is involved in the determination of the so-called diastatic powers, for which conditions only had optimal hydrogen-ion activities been established in the course of the earlier work of this Laboratory.

Experiments were therefore undertaken to establish the optimal hydrogen-ion activities for malt and pancreatic amylases when the temperature and time of enzymic hydrolysis were varied. The data obtained are discussed briefly below.

Experiments and Discussion

The experimental methods of measuring amylase activity have been described in detail in previous papers from this Laboratory.²

The slight reducing action of the substrate without enzyme was measured for each of the times, temperatures and hydrogen-ion activities

¹ We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

² Sherman and co-workers, *THIS JOURNAL*, 41, 231 (1919); 32, 1073 (1910); 42, 2461 (1921); 37, 623 (1915).

studied, and used as a correction in reporting the enzymic activities. The hydrogen-ion activities reported in this paper were determined electrometrically in portions of the actual substrate systems used.

Malt Amylase in the Presence of Phosphates.—The experiments with malt amylase were carried out both with extracts of barley malt prepared in a uniform manner and with a purified preparation which had been obtained according to the method of Sherman and Schlesinger and these two forms of the enzyme gave essentially concordant results. In the earlier series of these experiments, the enzyme was allowed to act upon starch solutions containing 0.06 *M* dihydrogen phosphate and adjusted to a systematic series of Sørensen values at close intervals from *P_H* 4.0 to *P_H* 6.0. The time was varied from one-half hour to two hours and the temperature from 30 to 70°. These experiments showed that as the temperature of the hydrolysis is increased, malt amylase becomes more sensitive to changes in the hydrogen-ion activity of its environment. Also the enzyme exerted its optimal activity in less acid solutions as the temperature of the hydrolysis was increased. Thus malt amylase exerted its optimal activity under the conditions of these experiments in solutions adjusted at room temperature to Sørensen values of *P_H* 4.4 to 5.0 at 30 and 40°; of 4.6 to 5.0 at 50°; of 5.2 to 5.5 at 60° and of 5.3 to 5.8 at 70°. With the purified preparation the zone of optimal activity was slightly narrower, *P_H* 4.6 to 4.8 at 40° and 5.3 to 5.4 at 60°.

At any given temperature, however, malt amylase exerts its activity under practically the same optimal conditions when the period of hydrolysis is varied from one-half to two hours.

Between the completion of this part of our experimental work and its preparation for publication, Olsen and Fine³ published the results of experiments with a mixture of wheat and malted barley flours in which also it was found that the enzyme exerts its optimal activity at different hydrogen-ion activities according to the temperature, and noted a greater influence of small changes of hydrogen-ion activity at the higher temperatures.

Electrometric Measurements at Temperatures of Enzyme Experiments.—The electrometric measurements of the solutions so far considered were made at room temperature and calculated with the usual temperature corrections to Sørensen or *P_H* values.⁴ As shown above, these values were found to differ markedly for those solutions which enable malt amylase to exert its optimal activity at the different temperatures. The question therefore arose as to whether the hydrogen-ion activities of the starch solutions measured at room temperature are also the hydrogen-

³ Olsen and Fine, *Cereal Chemistry*, 1, 215 (1924).

⁴ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, 1923, 2nd ed., pp. 457, 459.

ion activities of the solutions during hydrolysis. To answer this question e.m.f. measurements were made at the higher temperatures as well as at room temperature upon starch solutions (substrate systems) made up exactly as were those which had been found to afford the most favorable conditions for the amylase activity at each temperature. The P_H values were calculated according to the equation e.m.f. (saturated calomel) — e.m.f. (obs.) = $0.000198T \log(C_{H^+}/10^{-4.72})$, where $0.000198T \log(C_{H^+}/10^{-4.72})$ is the electrode potential for hydrogen at atmospheric pressure⁵ and where 0.5266 is⁶ the e.m.f. of the saturated calomel cell at 25°. The calomel cell was of the type described by Wilson and Kern⁷ and could not conveniently be immersed in the thermostat. There would, therefore, be a slight Peltier effect which would cause some error in the above calculations but which would not be significant in the changes in which we are interested here. The e.m.f. observed was corrected for barometric pressure by use of the equation,⁴ $E_{\text{bar.}} = (0.000198T/2) \log(760/x)$, where x is the barometric pressure minus the vapor pressure of water at the temperature under consideration. This correction was added to the observed e.m.f. in the above equation.

The results are given in Table I and show that the e.m.f. and Sørensen values obtained with a given solution measured at the lower and higher temperatures are not markedly different and that the measurements made at room temperature are also a measure of the hydrogen-ion activities of the substrates at the temperatures of hydrolysis. This would seem to indicate that malt amylase exerts its optimal activity under different conditions of hydrogen-ion activity at different temperatures.

TABLE I
INFLUENCE OF TEMPERATURE UPON E.M.F. OF THOSE SOLUTIONS WHICH ENABLE
MALT AMYLASE TO EXERT ITS OPTIMAL ACTIVITY AT 30, 50, 60 AND 70°

Temps. of enzymic hydrolyses °C.	Electrometric Measurements and Sørensen Values					
	At room temperature			At temperatures of enzymic hydrolyses		
	E.m.f. ^a	Temperature of e.m.f. reading, °C.	Corre- sponding P _H value ^b	E m.f. ^a	Temperature of e.m.f. reading, °C.	Corre- sponding P _H value ^b
30	0.5137	24	4.53	0.5158	30	4.56
50	.5292	26	4.76	.5290	50	4.79
60	.5598	25	5.28	.5564	60	5.22
70	.5800	24.5	5.62	.5745	70	5.50

^a The barometric reading for the above e.m.f. values was 761.

^b Calculated as explained in the text.

Malt Amylase in the Presence of Acetate-Acetic Acid Mixtures.—In view of the work of Chrzaszcz, Bidzinski and Krause⁸ and of the more

⁵ Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925, p. 257.

⁶ Fales and Mudge, *THIS JOURNAL*, **42**, 2434 (1920).

⁷ Wilson and Kern, *Ind. Eng. Chem.*, **17**, 74 (1925).

⁸ Chrzaszcz, Bidzinski and Krause, *Biochem. Z.*, **160**, 155 (1925).

recent work of Luers and Nichimura,⁹ we have carried out a second series of experiments with malt amylase under the same conditions described for the first series, except that we used 0.01 *M* sodium acetate-acetic acid buffer mixtures instead of phosphate to regulate the hydrogen-ion activities of the substrates. It was found that in the presence of acetate and in experiments of the same duration, malt amylase exerts its optimal activity at 40° and at 60° in solutions of about *P_H* 4.6 for half an hour and at about *P_H* 4.8 for two-hour periods of hydrolysis. This confirms the findings of Luers and Nichimura and indicates that the effects of acetate and phosphate are somewhat different in this respect. The enzyme is more sensitive to changes in the hydrogen-ion activity of its environment at the higher temperature, whether it acts in the presence of phosphate or of acetate, but in the presence of acetate there is a tendency for the optimal enzymic activity to occur in slightly less acid solutions as the experimental period is lengthened.

Within the range covered by our experiments, heat does not appreciably influence the hydrogen-ion activities of our systems. This is shown for the phosphate solutions by the experiments summarized in Table I and has also been experimentally demonstrated for the acetate solutions. Thus the e.m.f. value of the starch solution, containing 0.01 *M* acetate, which permitted malt amylase to exert its optimal activity at 60° was 0.5215 (or *P_H* 4.65) when measured at 23.5° and 0.5240 (or *P_H* 4.72) when measured at 60°, the temperature of the hydrolysis.

Parallel hydrolyses of the phosphate and acetate substrates carried out at 60°, with determinations of the hydrogen-ion activities of the solutions before and after the hydrolyses, showed that neither of the solutions had changed in hydrogen-ion activity during the experiment.

Pancreatic Amylase.—Experiments similar to those described with malt amylase were also carried out with pancreatic amylase, measuring both its saccharogenic and amylolytic activities. Starch solutions, two per cent. for the former and one per cent. for the latter measurements, were adjusted to Sørensen values systematically varied at close intervals from *P_H* 6.3 to *P_H* 7.7. The enzymic activity was measured in periods of one-half, one and two hours at 30 to 70°.

In the first series of experiments, a commercial pancreatin was used in the presence of 0.05 *M* sodium chloride and 0.0005 *M* disodium phosphate. In the second series of experiments a purified enzyme preparation obtained according to the method of Sherman and Schlesinger was used in the presence of 0.03 *M* sodium chloride and 0.01 *M* phosphate mixtures which had very recently been found¹⁰ to afford slightly more satisfactory conditions.

⁹ Luers and Nichimura, *Wochenschrift für Brauerei*, 43, No. 38, p. 415-416, Sept., 1926.

¹⁰ Adams, *Dissertation*, Columbia University, 1927.

The results of the two series of experiments are in agreement and show that under these conditions the hydrogen-ion activities for the optimal enzymic activity expressed as Sørensen values were P_H 7.0 to P_H 7.2 for one-half to two hours at 30 to 50°, P_H 6.9 for half an hour and P_H 6.7 for two-hour periods at 60°. The rapid destruction of the enzymic activity at 70° made it difficult to obtain any satisfactory results at this temperature.

This difference between the hydrogen-ion activities for the optimal activity of pancreatic amylase at the lower temperatures and at 60°, while very slight, appears to be a true difference and not due to the influence of heat on the hydrogen-ion activities of the solutions themselves, for the hydrogen-ion activity of the solution affording optimal enzymic activity at 60° was found to be the same when measured at room temperature and at 60°.

Summary

As the temperature of hydrolysis is increased from 30 to 70°, malt amylase exerts its optimal activity at different hydrogen-ion activities when acting in the presence of 0.06*M* phosphate mixtures; whereas, in the presence of 0.01*M* acetate-acetic acid mixtures, this amylase exerts its optimal activity in solutions of the same hydrogen-ion activity at the different temperatures.

In the presence of 0.06 *M* phosphate, the hydrogen-ion activities of the solutions affording optimal activity of the enzyme did not show appreciable change as the experimental period was lengthened from one-half to two hours at any given temperature (within the range 30–60°) while in the presence of 0.01 *M* acetate there is a tendency for the enzyme to exert its optimal activity in slightly less acid solutions as the period of hydrolysis is increased.

The difference in the behavior of the enzyme in the presence of phosphate and of acetate has been shown by e.m.f. measurements of the solutions at room temperature and at the temperatures of hydrolysis, and by measurements before and after hydrolysis, not to be due to the influence of heat or of the products of hydrolysis upon the hydrogen-ion activities of the solutions themselves.

Whether in the presence of phosphate or of acetate, a higher temperature seems to render malt amylase more sensitive to changes in the hydrogen-ion activity of its environment.

Pancreatic amylase, in experiments of one-half to two hours at 30–50°, exerted its optimal activity at P_H 7.0–7.2; but in experiments at 60° the optimal activity for half-hour periods was found at P_H 6.9 and for two-hour periods at P_H 6.7.

From the standpoint of accurate investigation of enzyme action, the results here reported upon two typical amylases indicate that the factors

which induce optimal enzymic activity are even more dependent upon each other than has previously been realized and that none of them should be regarded as fixed if any of the others is changed.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

CATALYTIC OXIDATIONS IN AQUEOUS SOLUTIONS

I. THE OXIDATION OF FURFURAL

BY NICHOLAS A. MILAS¹

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Introduction

The present investigations are part of the applications of catalysts such as osmium tetroxide, vanadium pentoxide, etc., to the oxidation of organic compounds by means of chlorates.

In previous communications² it has been shown that small quantities of osmium tetroxide can induce the oxidation of relatively large quantities of organic substances by means of chlorates. The use of vanadium pentoxide with chlorates has been heretofore limited only to a very few special cases³ in which vanadium salts were used rather than the oxide in the presence of strong acids. The present paper describes several experiments in which vanadium pentoxide has been successfully used in neutral as well as in dilute acid solutions to induce the oxidation of furfural and pyromucic acid by means of chlorates.

Furfural has been oxidized with dil. potassium permanganate solution to pyromucic acid by Volhard,⁴ with bromine water at the temperature of the water-bath to mucobromic acid by Simonis,⁵ with hydrogen peroxide in the presence of ferrous salts to δ -hydroxyfurfural by Cross, Bevan and Heiberg,⁶ and with Caro's acid to succinic acid by Cross, Bevan and Briggs.⁷

In the Experimental Part, it will be shown that with a mixture of sodium chlorate and small quantities of osmium tetroxide in dilute acid solution, furfural yields principally mesotartaric acid, while fumaric acid is the chief product formed when the reaction is carried out in neutral solution with osmium tetroxide replaced by vanadium pentoxide. Similar results

¹ National Research Fellow in Chemistry.

² (a) Milas and Terry, *THIS JOURNAL*, **47**, 1414 (1925). (b) Terry and Milas, *ibid.*, **48**, 2647 (1926).

³ Guyard, *Bull. soc. chim.*, [2] **25**, 58 (1876); *Chem. News*, **33**, 70 (1876). Willstätter and Dorogi, *Ber.*, **42**, 4128 (1909).

⁴ Volhard, *Ann.*, **261**, 379 (1891).

⁵ Simonis, *Ber.*, **32**, 2084 (1899).

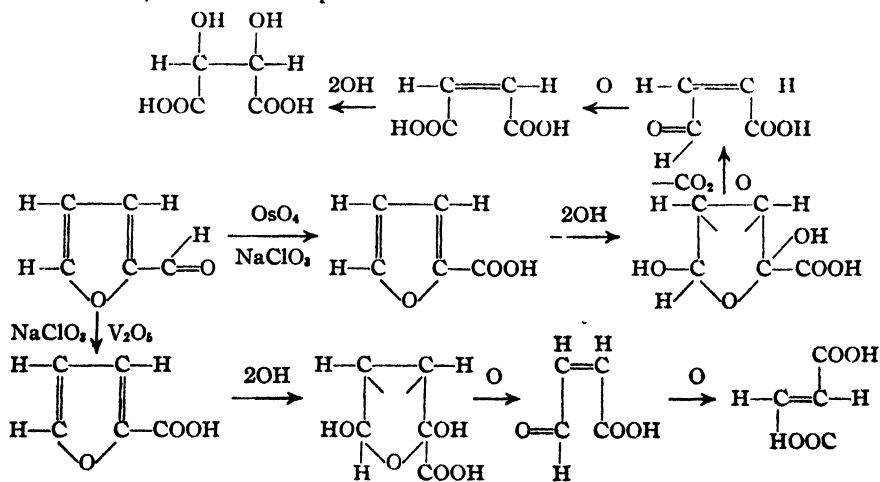
⁶ Cross, Bevan and Heiberg, *J. Chem. Soc.*, **75**, 747 (1899).

⁷ Cross, Bevan and Briggs, *Ber.*, **33**, 3132 (1900).

but lower yields of the principal products were obtained when pyromucic acid was used instead of furfural.

These results are not at all surprising but quite in accordance with the classical researches of Hill and his co-workers on the structure of the furane ring. Hill and Sanger⁸ have shown that pyromucic acid is slowly oxidized with bromine water first to fumaryl aldehyde, then at low temperatures to maleic acid or, at higher temperatures, to fumaric acid. More striking results were obtained by Hill and Hartshorn⁹ who found that α,δ -dibromofurane, prepared from δ -bromopyromucic acid, oxidizes to give, in the cold, maleic acid and at higher temperatures fumaric acid, hydrogen bromide being given off in both cases. Obviously hydroxylation of the conjugated system of the furane ring occurred first on the α,δ -carbon atoms followed by splitting of hydrogen bromide and subsequent hydrolysis of the maleic anhydride. At higher temperatures hydrolysis of maleic anhydride and transmutation of maleic acid to fumaric acid may occur simultaneously.

A similar mechanism may be adopted to explain the catalytic oxidation of furfural. Although no pyromucic acid was isolated, furfural must first be oxidized to this acid. In the reactions studied, there are two distinct stages of each reaction, a violent followed by a mild reaction. This is particularly true in the oxidation of furfural with vanadium pentoxide and sodium chlorate in which the temperature rises during the violent reaction from 70 to 105°. Furthermore, carbon dioxide is evolved in greater quantities during the violent stage. In addition to the temperature effect in this last case, considerable quantities of chlorine dioxide are formed, which are responsible for the transmutation of maleic acid as



⁸ Hill and Sanger, *Proc. Am. Acad.*, **21**, 144 (1885-6).

⁹ Hill and Hartshorn, *Ber.*, **18**, 448 (1885).

soon as it is formed. This view has been substantiated by actual experiments in which maleic acid was transmuted, in aqueous solution, to the extent of 10% in eight hours at 70 to 75° by the mixture of vanadic oxide and sodium chlorate. The mechanism of the principal reactions, therefore, might be best expressed as shown on the preceding page.

This mechanism seems, to the author, the most probable, although other mechanisms are possible. So far, attempts to isolate the dihydroxypyromucic acid failed, due perhaps to its extreme instability. However, maleic acid aldehyde has been actually isolated as the intermediate product of the reaction. Several investigators have already shown that when pyromucic acid is carefully oxidized in water or alkaline solution with bromine,¹⁰ or with oxygen¹¹ in presence of light, maleic acid aldehyde is formed.

Experimental Part

Oxidation of Furfural with Sodium Chlorate and Vanadium Pentoxide

Materials Used.—Two grades of furfural were used, the c. p. grade and the technical grade, both furnished by the Eastman Kodak Company.

The sodium chlorate used was the u. s. p. grade furnished by Merck.

Preparation of the Catalyst.—Twenty g. of c. p. ammonium metavanadate was suspended in 200 cc. of water and to this was added slowly 30 cc. of concd. hydrochloric acid (d., 1.90). The reddish-brown semi-colloidal precipitate was washed several times with water by decantation and finally suspended in 300 cc. of water and allowed to stand at room temperature for three days. This treatment made the precipitate almost granular and easy to filter. The precipitate was then collected on filter paper by means of the pump, washed several times to free it from hydrochloric acid and dried for 12 hours at 120°. To free it completely from occluded hydrochloric acid, it was finely powdered and dried again at 120° for 12 hours longer; yield of the dried oxide, 11 g. The catalyst thus prepared is very active for all purposes of oxidations with chlorates.

The Reaction.—Preliminary experiments showed that sodium chlorate in aqueous solution without the aid of the catalyst does not oxidize furfural even if the solution is made acid or heated to the boiling point of water. However, vanadium pentoxide in the absence of chlorate oxidizes furfural and shows the following changes of color:¹² V_2O_5 (yellow) $\rightarrow V_2O_4$ (blue) $\rightarrow V_2O_3$ (green). These color changes are instantly reversed when a small crystal of chlorate is added to the solution and reappear when

¹⁰ (a) Schmelz and Beilstein, *Ann. Suppl.*, 3, 279 (1865). (b) Limpricht, *Ann.*, 165, 285 (1873). (c) Hill and Allen, *Am. Chem. J.*, 19, 650 (1897). (d) Fecht, *Ber.*, 38, 1272 (1905).

¹¹ Ciamician and Silber, *Ber.*, 46, 1563 (1913).

¹² T. F. Rutter [*Dissertation*, Leipzig, 1904] has shown that salts of vanadium tetroxide are blue and those of vanadium trioxide are green.

the chlorate is completely reduced to the chloride. Ordinarily, when chlorate is present in excess, vanadium pentoxide does not undergo the above color changes and the reaction appears to take place entirely on its surface. As the acidity of the solution rises, due to the organic acids produced as a result of the oxidation, vanadium pentoxide goes slowly into solution and is held there, perhaps in the colloidal state. One therefore may easily conceive that vanadium pentoxide acts as an "oxygen carrier" in inducing the oxidation of organic compounds by means of chlorates.

The general procedure as finally adopted was as follows.

Forty-six g. of sodium chlorate, 0.2 g. of vanadium pentoxide and 100 cc. of water were placed in a 500cc. Erlenmeyer flask which was connected to a condenser and a dropping funnel with a two-hole rubber stopper. The mixture was heated to 70–75° by supporting the flask 10 cm. above a hot electric plate. This arrangement was very satisfactory in keeping the temperature constant to within 3°. Twenty g. of furfural was then slowly dropped into the solution at the rate of about 0.5 g. per minute, and allowed to undergo the violent reaction. During this reaction the temperature of the solution rises to 105° and a rapid evolution of carbon dioxide takes place. If the addition of furfural is too rapid the reaction becomes too violent and almost uncontrollable; if it is too slow the fumaric acid formed is further oxidized to oxalic acid and thence to carbon dioxide and water. The violent reaction lasts from 50 to 75 minutes. At the end of a definite number of hours, the reaction was stopped, the flask disconnected, stoppered and allowed to stand at room temperature overnight. The fumaric acid which separated was collected on the filter paper, washed once with cold water, dried and weighed. This acid is fairly pure; m. p., 282–284° in a sealed tube. After one recrystallization from hot water, the melting point rose to 285–287° and remained unaltered on further recrystallizations.

Anal. Subs., 0.2881: CO₂, 0.4342; H₂O, 0.0910. Calcd. for C₄H₄O₄: C, 41.37; H, 3.44. Found: C, 41.11; H, 3.51.

Titration with sodium hydroxide. Subs., 0.2606, 0.1957; required 43.54, 32.50 cc. of 0.1037 *N* NaOH (phenolphthalein). Calcd. for C₄H₄O₄: 43.33, 32.52 cc.

The last two experiments of Table I show the influence of a 2% solution of sulfuric acid on the speed of the reaction as well as on the yield of fumaric acid. The reaction, however, is much too violent to be of practical use.

TABLE I
VARIATION OF YIELD OF FUMARIC ACID WITH TIME OF HEATING

Expt.	1	2	3	4	5 ^a	6 ^b	7 ^{a,b}
Time of heating, hrs.	22	16	12.5	7	8	4.5	3
Fumaric acid, yield, %	51.7	70.3	77.8	64.1	66.2	72.4	70.0

^a Technical furfural was used in these experiments.

^b The water used was replaced with 2% sulfuric acid.

It will be seen from Table I that the maximum yield of fumaric acid, assuming that all furfural is oxidized to this acid, was obtained when the reaction mixture was heated for 12.5 hours.

Treatment of the Filtrate.—The filtrate of Expt. 4 shown in Table I was boiled with an excess of barium carbonate for two hours, cooled, and then filtered by means of

the pump. The filtrate was treated with two volumes of 95% alcohol; a white, semi-granular precipitate formed. This was collected on the filter paper and dried at room temperature; yield, 9.3 g. Since this salt was more soluble in hot than in cold water, it was recrystallized twice from this solvent and dried in a vacuum desiccator over concd. sulfuric acid for several days.

Anal. Subs., 0.2873, 0.2132, 0.2812; BaSO₄, 0.2211, 0.1664, 0.2195. Calcd. for C₈H₂O₆Ba.H₂O: Ba, 46.2. Found: 45.32, 45.94, 45.95.

Determination of water. Subs., 0.4504, heated at 150–160° to constant weight; H₂O, 0.0241. Calcd. for C₈H₂O₆Ba.H₂O: H₂O, 6.05. Found: 5.36.

Combustion of the barium salt. Here the assumption is made that all barium is converted to barium carbonate and the percentage of carbon is calculated accordingly. Subs., 0.2745, CO₂, 0.1939; H₂O, 0.0365. Calcd. for C₈H₂O₆Ba.H₂O: C, 20.16; H, 1.36. Found: C, 19.57; H, 1.48.

The empirical formula of this acid, therefore, is C₈H₄O₆. Work is now in progress to determine its structure.

Isolation of Maleic Acid Aldehyde.—An experiment was then performed in the usual way except that it was stopped at the end of the violent reaction. The reaction mixture was cooled in ice and the solid which separated was dried and weighed; yield of fumaric acid, 6 g. The filtrate was shaken with 500 cc. of ether and the ether extract dried for several days over anhydrous sodium sulfate. When the ether was distilled the residue consisted of a mixture of a thick, brownish oil of a very penetrating odor and a whitish solid which proved to be fumaric acid. The oil is very unstable and decomposes when heated with water on the water-bath, to give fumaric acid. The ether extraction, however, is not efficient and the original aqueous solution was found to contain large quantities of maleic acid aldehyde, which gives a rich orange-reddish color in water when heated on the water-bath with a few drops of an alcoholic solution of phloroglucinol. The phenylhydrazone derivative of this aldehyde was then prepared as follows. The original aqueous solution was neutralized with sodium carbonate (litmus), cooled in ice and phenylhydrazine added in excess. A yellowish-brown precipitate was formed which became deep yellow upon the addition of dil. acetic acid. The precipitate was quickly removed from the solution mixture, dried and weighed; yield, 11 g. When recrystallized twice from hot benzene, it yielded crystals (needles under the microscope); m. p., with decomposition, 157.5–158°. Fecht^{10d} describes the same substance having a melting point of 158–159°.

Anal. Subs., 0.1297, 0.2295; N₂, 16.5 cc. (18°, 759 mm.), 28.6 cc. (18°, 759.5 mm.) (over 50% KOH).

Calcd. for C₁₀H₁₀O₂N₂: N, 14.74. Found: 15.04, 14.71.

Oxidation of Pyromucic Acid with Sodium Chlorate and Vanadium Pentoxide

Pyromucic acid was prepared according to Wilson.¹³ It was purified by recrystallization from a hot mixture of two parts of carbon tetrachloride and one part of chloroform, and melted at 132–133°.

Five g. of pyromucic acid, 9 g. of sodium chlorate, 0.08 g. of vanadium pentoxide and 25 cc. of water were brought together in a 250cc. Erlenmeyer flask which was connected to a reflux condenser. The mixture was heated at 70–75° for eight hours, then cooled and the solid, 3.5 g., separated and dried. Since this appeared to be a mixture of unoxidized pyromucic and fumaric acids, it was treated with a small volume of ether,

¹³ Wilson, "Organic Syntheses," John Wiley's Sons and Co., 6, 44, (1926).

which extracted the former. The residual solid was recrystallized twice from hot water; m. p., 284 to 286° in a sealed tube; yield, 1 g. The presence of small quantities of oxalic acid was detected in the original mixture by the calcium oxalate test, but no attempt was made to isolate any other acid.

Oxidation of Furfural with Sodium Chlorate and Osmium Tetroxide

The catalyst was prepared according to Milas and Terry.^{2a} Preliminary experiments showed that osmium tetroxide, without the presence of chlorates, oxidizes furfural and forms a dark film of one of its lower oxides which adheres to the furfural and is not readily reoxidized by the addition of a solution of sodium chlorate. An experiment run continuously for a week at 50° in a thermostat failed to show an appreciable diminution of volume of the furfural layer. However, when the water used was replaced with an equivalent volume of a solution of 0.1 *N* hydrochloric acid furfural was oxidized, at first rapidly, then slowly to mesotartaric and oxalic acids. The following procedure was finally adopted.

Fifty-five g. of sodium chlorate, 10 cc. of a 0.98% solution of osmium tetroxide, 260 cc. of water and 30 cc. of about a 1 *N* solution of hydrochloric acid were brought together in a 500cc. Erlenmeyer flask connected to a reflux condenser and a dropping funnel. The mixture was brought to 50° in a thermostat, then 20 g. of pure furfural was dropped into it at the rate of about 5 cc. for every 30 minutes. The solution was heated until the odor of furfural had almost completely disappeared. This took 110 hours. At the end of this period of time, the solution was cooled and shaken with 200 cc. of benzene to extract the catalyst. The water layer contained tartaric and oxalic acids and was neutralized with dil. ammonium hydroxide (litmus), brought to boiling, then treated with a 10% solution of calcium chloride and allowed to stand overnight. The precipitate, which had separated was collected, dried and weighed; yield, 28.3 g. This was extracted with a 20% solution of sodium hydroxide, the extract neutralized with hydrochloric acid (litmus) and allowed to stand overnight. The calcium mesotartrate was then collected, dried and weighed; yield, 24.5 g. or 48.7% of mesotartaric acid.

Anal. Subs., 0.4603, 0.4456. CaO, 0.1087, 0.1048. Calcd. for $C_4H_4O_6Ca \cdot 3H_2O$: Ca, 16.53. Found: 16.87, 16.79.

Determination of water. Subs., 0.5889. H_2O , 0.1301. Calcd. for $C_4H_4O_6Ca \cdot 3H_2O$: H_2O , 22.30. Found: 22.09.

Titration of the free acid with sodium hydroxide. Subs., 0.3306, 0.3353; required 38.25, 38.76 cc. of 0.1037 *N* NaOH (phenolphthalein). Calcd. for $C_4H_4O_6 \cdot H_2O$: 37.95, 38.49 cc.

The residual salt from the sodium hydroxide extraction was reprecipitated once, dried and analyzed.

Anal. Subs., 0.5929. CaO, 0.2275. Calcd. for $C_4O_6Ca \cdot H_2O$: Ca, 47.41. Found: 47.42.

Oxidation of Pyromucic Acid with Sodium Chlorate and Osmium Tetroxide

Five g. of pyromucic acid, 5 g. of sodium chlorate, 2 cc. of osmium tetroxide solution, and 25 cc. of water were brought together in a 250cc. Erlenmeyer flask fitted with a reflux condenser. The mixture was heated at 50° in a thermostat for 60 hours. The experiment yielded 4 g. of calcium mesotartrate and 0.5 g. of calcium oxalate.

In conclusion, I wish to express my sincere thanks to Professors H. S. Taylor and L. W. Jones for their invaluable suggestions in this research.

Summary

1. Vanadium pentoxide induces the oxidation of furfural and pyromucic acid with chlorates to give fumaric acid as the principal product.
 2. Osmium tetroxide also induces the oxidation of furfural and pyromucic acid with chlorates to give mesotartaric acid as the principal product and oxalic acid as the by-product.
 3. The mechanism of the reaction has been worked out and malic acid aldehyde has been isolated as the intermediate product.
 4. An acid having the empirical formula $C_5H_4O_6$ has also been isolated.
- PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 548]

RESEARCHES ON SELENIUM ORGANIC COMPOUNDS.

VII. THE SYNTHESIS OF 2-PHENYL-, 2-FURYL- AND 2-THIENYL-BENZOSELENAZOLES, OF 2-PHENYL-BENZOSELENAZOLE-4'-ARSONIC ACID AND OF OTHER BENZOSELENAZOLES¹

BY MARSTON TAYLOR BOGERT AND ARTHUR STULL²

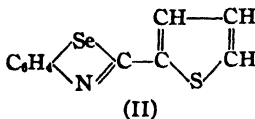
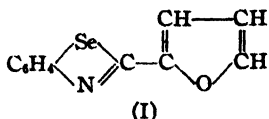
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Nitro-, amino- and hydroxy-phenyl-benzoselenazoles have been synthesized by methods entirely analogous to those developed in these Laboratories for the corresponding benzothiazoles, by condensing the zinc *o*-aminoselenophenolate with the appropriate aldehyde or acid halide. As was expected, these compounds proved rather more difficult to prepare and less stable than their sulfur analogs.

Perhaps the most remarkable result of these syntheses is the persistence of the "Rosenkoerper" odor of 2-phenyl-benzothiazole even when the thiazole sulfur is replaced by selenium and the phenyl by a furyl or thienyl group. The odor of the dry compounds at ordinary temperature is faint, but when heated or in solution is of pronounced geranium or tea-rose type.

Further, these furyl (I) and thienyl (II) derivatives present new and



interesting combinations of dissimilar heterocyclic systems, which offer

¹ That portion of this paper which deals with the arsonic acid was presented at the Washington Meeting of the National Academy of Sciences, April 26, 1926. The other syntheses were reported to the Division of Organic Chemistry of the American Chemical Society, at the Philadelphia Meeting, September 8, 1926.

² Research Assistant, Columbia University, for the academic year 1925-1926.

opportunities of determining differences in the behavior of the cycles when attacked by various reagents.

Through the courtesy of Dr. Francis Carter Wood, Director of the Crocker Institute of Cancer Research, the sodium salt of the arsonic acid was tested, by intravenous injection, on mice and rats. It proved to be quite toxic to the host and without curative action on tumor growths in these animals. For healthy mice weighing 14–18 g. the lethal dose was 0.00025 g. and for rats of 40–50 g. the maximum tolerated dose was 0.00075 g. Its action upon various pathogenic microorganisms also will be investigated.

Experimental Part

***o*-Nitrophenyl Diselenide, $(\text{O}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$.**—The method of Bogert and Andersen³ was varied in several particulars, and the following process was found to give the best results.

A mixture of 25 g. of sodium selenide in 250–300 cc. of 95% alcohol was refluxed until a clear solution was obtained, when 16 g. of finely pulverized metallic selenium⁴ was added and the refluxing continued for half an hour longer. This dark reddish-brown solution was gradually stirred into a warm solution of 50 g. of commercial *o*-nitrochlorobenzene in 100 cc. of alcohol and the mixture was refluxed for two to three hours additional. The use of a slight excess of sodium diselenide was found advantageous. As the hot solution cooled, the nitrophenyl diselenide separated. It was removed, washed thoroughly with water and with alcohol, and then formed a greenish-brown microcrystalline solid; yield, 37 g., or 57%. Recrystallized from glacial acetic acid to the constant melting point of 209° (corr.), it appeared as a pale brownish microcrystalline solid, readily soluble in benzene. Bogert and Andersen reported a melting point of 206.2–206.5° (corr.) for their product; Bauer,⁵ who prepared it by a different method, found 209°.

***o*-Aminoselenophenol, $\text{H}_2\text{NC}_6\text{H}_4\text{SeH}$.**—From the nitrophenyl diselenide, the zinc salt of the aminoselenophenol was obtained by the method of Bogert and Andersen.³ When a carefully purified nitro diselenide was used, the yield of zinc salt was 81%; with a crude diselenide, 55%. The product in the latter case also was found suitable for further syntheses.

As it separates first, the pure zinc salt is practically colorless, but it rapidly turns yellow and then brown in the light. Our observation in this matter is therefore at variance with that of Bauer,⁵ who prepared the salt in another way and reported that it was stable in the air.

2-Phenyl-benzoselenazole, $\text{C}_6\text{H}_4 \begin{array}{c} \text{Se} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CC}_6\text{H}_5$, was synthesized from

the zinc salt of *o*-aminoselenophenol and benzoyl chloride, as described by

³ Bogert and Andersen, *Proc. Nat. Acad. Sci.*, 11, 217 (1925).

⁴ The selenium used in this investigation was supplied by the Baltimore Copper Smelting and Rolling Co., through the courtesy of E. W. Rouse, Jr., General Superintendent, for whose assistance we are most grateful.—M. T. B.


⁵ Bauer, *Ber.*, 46, 92 (1913).

Bauer⁵ and modified by Bogert and Andersen,³ pale, straw-colored needles, m. p. 117.5° (corr.), in agreement with the literature^{3,5,6}; yield, 70%.

Anal. Calcd. for C₁₃H₉NSe: C, 60.14; H, 3.48; Se, 30.67. Found: C, 61.51, 62.71; H, 3.28, 3.76; Se, 30.38.

NITRO-, AMINO-, AND HYDROXY-BENZOSELENAZOLES

Derivative	Yield, %	M. p. (corr.), °C.	Se calcd., %	Se found, %	C and H, %
2- <i>m</i> -nitro	67	148	26.12	25.91	
2- <i>p</i> -nitro	71	211	26.12	...	{ Calcd.: C, 51.45; H, 2.64. Found: C, 51.88, 51.78; H, 3.08, 2.73
2- <i>o</i> -amino	..	142.5	28.98	28.80	
2- <i>m</i> -amino	77	159.5	28.98	28.87	
2- <i>p</i> -amino	98	156	28.98	28.54	
2- <i>o</i> -hydroxy	23	131	28.88	28.60	
2- <i>p</i> -hydroxy	46	223	28.88	28.36	

2-(*p*-Nitrophenyl)-benzoselenazole, C₆H₄CC₆H₄NO₂(*p*).—An intimate mix-

ture of finely pulverized zinc *o*-aminoselenophenolate (1 mole) and *p*-nitrobenzoyl chloride (2 moles) was fused for an hour at 100°. The reaction began at about the melting point of the chloride (71–73°). The cooled melt was pulverized, washed with water to remove zinc salts and with sodium carbonate to eliminate any *p*-nitrobenzoyl chloride or *p*-nitrobenzoic acid. Sodium hydroxide solution is not suitable, since it dissolves some of the selenazole also. The crude yellow product was decolorized and crystallized from glacial acetic acid until the melting point remained constant at 211° (corr.). The crystals, when finally washed with a little alcohol and dried at 100°, appeared in minute, pale yellow, lustrous, short needles.

2-(*m*-Nitrophenyl)-benzoselenazole was prepared in the same way as the *p*-nitro isomer, and the reaction began as soon as the *m*-nitrobenzoyl chloride melted (about 35°). The crude product was crystallized from glacial acetic acid by adding three volumes of water to the hot solution, and was then recrystallized from 95% alcohol until the melting point remained constant at 148° (corr.). Further crystallizations from glacial acetic acid, ethyl acetate, acetone or benzene failed to change this melting point. In appearance, the pure compound resembled its *p*-nitro isomer, except that it was much paler in color.

2-(*o*-Nitrophenyl)-benzoselenazole.—Attempts to get this isomer pure have proved futile so far, but a crude product was obtained which yielded the pure *o*-aminophenyl-benzoselenazole upon reduction.

When zinc *o*-aminoselenophenolate and *o*-nitrobenzoyl chloride were brought together, even at temperatures near 0°, an explosion occurred with separation of carbon and zinc oxide. This is entirely similar to the experience of Smidth⁷ on bringing together the same chloride with the zinc *o*-aminothiophenolate.

When the zinc salt and nitrobenzoyl chloride were allowed to interact in glacial acetic acid solution, a yellow, gummy product separated which, after washing with water and with sodium carbonate, still contained zinc in apparent chemical combination. All attempts to isolate from this any pure compounds failed. It was therefore reduced

⁵ Fromm and Martin, *Ann.*, **401**, 178 (1913). Bogert and Chen, *THIS JOURNAL*, **44**, 2355 (1922).

⁷ Smidth, *Dissertation*, Columbia University, 1925, p. 31.

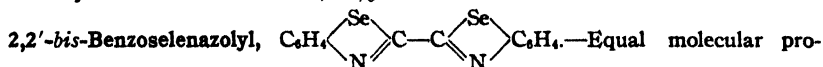
directly, by tin and dil. hydrochloric acid, to the 2-(*o*-aminophenyl)-benzoselenazole, in much the same way as described for the following *m*- and *p*-amino isomers. Recrystallized from 75% alcohol to the constant melting point of 142.5° (corr.), it formed minute, pale greenish-yellow, lustrous scales, whose alcoholic solution exhibited no fluorescence; yield, 1.5 g. from 4 g. of the crude initial material.

2-(*m*-Aminophenyl)-benzoselenazole.—A mixture of 2 g. of the corresponding nitro derivative, 10 cc. of concd. hydrochloric acid, 90 cc. of water and 10 g. of granulated tin was boiled for three hours. Complete solution of the nitro derivative ensued within less than two hours. The hot filtrate from the excess of tin was stirred gradually into an excess of 4*N* sodium hydroxide solution, which precipitated the amine. After this alkali mixture had been kept warm for several hours, it was cooled and filtered. The crude amine was decolorized and crystallized from 50% alcohol, when it appeared in pale yellow, glassy needles, which dissolved in alcohol without fluorescence.

2-(*p*-Aminophenyl)-benzoselenazole was prepared in the same way as the *m*-amino isomer, and resembled it closely, except that the crystals were paler in color and their alcoholic solution exhibited a light violet fluorescence.

2-(*o*-Hydroxyphenyl)-benzoselenazole.—When a mixture of 1 g. of zinc *o*-aminoselenophenolate, 1 g. (an excess) of salicyl aldehyde and 125 cc. of glacial acetic acid was boiled for an hour, a clear, dark brown solution resulted. When left overnight at laboratory temperature, this solution deposited a small amount of zinc acetate and some metallic selenium. The filtrate from this deposit was diluted with three volumes of water, the curdy, brown precipitate separated and crystallized repeatedly from 50% alcohol; yield (after first crystallization from alcohol), 23%. The pure product formed fine, transparent needles of pale yellowish tinge, soluble in sodium hydroxide but not in sodium carbonate solution, and which gave no color reaction with ferric chloride either in aqueous or in alcoholic solution.

2-(*p*-Hydroxyphenyl)-benzoselenazole, produced similarly from the *p*-hydroxybenzaldehyde, using 0.6 g. of the aldehyde per gram of the zinc salt, formed larger and practically colorless, glassy needles, but in other respects resembled its *o*-isomer; yield, after one crystallization from alcohol, 46%.



The cooled and pulverized product was warmed with an excess of *N* sodium hydroxide solution, and the insoluble material was heated in a porcelain dish. A sublimate was obtained which crystallized from toluene in colorless, glistening scales, m. p. 314° (uncorr.), which gradually turned brownish on standing in the light and air.

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{Se}_2$: Se, 43.70. Found: Se, 43.74.



a suspension of 1 g. of 2-(*p*-aminophenyl)-benzoselenazole in 20 cc. of 2 *N* hydrochloric acid and 30 cc. of water, cooled to 0°, there was added slowly 0.5 g. of sodium nitrite dissolved in 10 cc. of water. The resulting solution, containing some suspended diazonium salt, was added to an ice-cold solution prepared from 5 g. of potassium arsenite, 50 cc. of water, 12 cc. of *N* sodium carbonate solution and 1 to 2 g. of copper bronze powder. The mixture was shaken from time to time, and tested periodically with litmus to make sure of its alkalinity. After standing for an hour at room temperature, it was heated at 100° until all frothing ceased (1 to 2 hours). During this heating, a slight odor was noted resembling that of 2-phenyl-benzoselenazole.

The alkaline mixture was filtered warm and the insoluble material was washed with a little warm sodium carbonate solution. The combined greenish filtrate and washings were acidified with concd. hydrochloric acid, the pale yellow, flocculent precipitate was removed, washed thoroughly with water and dried at 100°. Recrystallized from 50% alcohol, it formed microscopic, pale yellow scales, which melted with decomposition above 360°; yield, 27%. It dissolved readily in alcohol, but slightly in water, chloroform or acetone, and was practically insoluble in ethyl acetate or carbon disulfide. In alkali hydroxide or carbonate solution, it was easily soluble and was reprecipitated when these solutions were acidified.

Anal. Calcd. for $C_{12}H_{10}O_2NAsSe$: C, 40.82; H, 2.61; Se, 20.72; As, 19.61. Found: C, 42.62; H, 3.05; Se, 20.41; As, 17.80.

As these figures demonstrate, the analysis was a troublesome one, because of the particular elements present and the small amount of product isolated. Arsenic was determined as follows.

The substance was digested in a Kjeldahl flask with a small amount of concd. sulfuric acid and with additions of concd. nitric acid from time to time, to assist in the oxidation of the arsenic to arsenate. When the oxidation was complete, the colorless solution was diluted, made slightly ammoniacal, magnesia mixture added, then the whole was made strongly ammoniacal and left overnight. The precipitated magnesium arsenate was washed, dried and converted into pyro-arsenate.

A blank run in exactly the same way with 2-phenyl-benzoselenazole showed that no selenium was thrown down by magnesia mixture.

MONOSODIUM SALT—When the free arsonic acid and the calculated amount of 10% sodium hydroxide solution were brought together in absolute alcohol solution, the monosodium salt separated immediately as a fine, white solid, which was removed, washed thoroughly with absolute alcohol and dried; yield, practically that calculated. It is believed to be the first water-soluble organic selenium arsenic compound ever prepared.

2-(α -Furyl)-benzoselenazole (Formula I).—A mixture of one mole of zinc *o*-aminoselenophenolate with two moles of pyromucyl chloride was heated at 100° for 30 minutes, the cooled and pulverized melt extracted with *N* sodium hydroxide solution, to remove excess of acid chloride, and the residue decolorized and crystallized from 50% alcohol until the melting point remained constant at 133° (corr.). The compound formed colorless, glistening scales, with the characteristic agreeable odor of 2-phenyl-benzothiazole ("Rosenkoerper"); yield, 83%.

Anal. Calcd. for $C_{11}H_7ONSe$: C, 53.18; H, 2.82; Se, 31.90. Found: C, 54.20; H, 2.97; Se, 31.51.

2-(α -Thienyl)-benzoselenazole (Formula II), was prepared from the zinc *o*-aminoselenophenolate and α -thienyl chloride in much the same way as the α -furyl derivative just described. Decolorized and crystallized from 95% alcohol to the constant melting point of 114.5°, it was obtained in well-formed, glassy, lustrous prisms, of a pale greenish-yellow color, and with the same odor as the α -furyl derivative; yield, 60%. From 50% alcohol, it crystallized in smaller, practically colorless needles, of the same melting point. It is believed that this is the only organic compound known which contains both unoxidized sulfur and unoxidized selenium in its molecule and yet has an agreeable odor.

Anal. Calcd. for $C_{11}H_7NSe$: C, 49.99; H, 2.64; Se, 29.97. Found: C, 51.64; H, 2.86; Se, 30.15.

Analysis of Benzoselenazoles

So much difficulty was encountered in getting satisfactory carbon determinations in the combustion of these selenazoles, that in the case of many of the new products selenium was determined instead.

Bauer⁸ tested the methods of Frerichs,⁹ Becker and Meyer¹⁰ and Michaelis,¹¹ and found the latter the most satisfactory. It has the disadvantage, however, of requiring the use of sealed tubes.

We found that the following process gave very good results.

The sample (0.2–0.3 g.) was heated carefully in a small Kjeldahl flask with the minimum amount (8–10 cc.) of concd. sulfuric acid until a clear, colorless solution was obtained (4–7 hours). The cold acid solution was rinsed into a beaker, diluted to about 200 cc. and neutralized with concd. ammonium hydroxide solution. An excess (50–60 cc.) of concd. hydrochloric acid was added, the solution heated to boiling and saturated with sulfur dioxide. The selenium separated at first in the red, colloidal form but soon turned gray and precipitated. After standing overnight, the selenium was filtered out on a Gooch crucible, washed with water until free from chloride ion, then with a little alcohol, dried at 105°, and weighed as metallic selenium.

Summary

1. Zinc *o*-aminoselenophenolate yields the corresponding 2-nitro- or 2-hydroxyphenyl-benzoselenazoles when condensed with the proper nitro- or hydroxybenzaldehydes; with oxalyl chloride it gives the *bis*-benzoselenazolyl, and with pyromucyl and α -thienyl chlorides the α -furyl- and α -thienyl-benzoselenazoles, both of the latter possessing very agreeable odors.

2. From the nitro derivatives, the corresponding amines were obtained by reduction, and an arsonic acid from the 2-(*p*-aminophenyl) derivative by means of the Bart reaction.

3. The sodium salt of the arsonic acid was found to be without curative value when tested upon mouse tumors.

NEW YORK, N. Y.

⁸ Bauer, *Ber.*, **48**, 507 (1915).

⁹ Frerichs, *Arch. Pharm.*, **240**, 656 (1902). See also Price and Jones, *J. Chem. Soc.*, **95**, 1735 (1909). Vanino and Schinner, *J. prakt. Chem.*, [2] **91**, 123 (1915).

¹⁰ Becker and Meyer, *Ber.*, **37**, 2551 (1903).

¹¹ Michaelis, *Ber.*, **30**, 2827 (1897). Michaelis and Langenkamp, *Ann.*, **404**, 27 (1914).

[CONTRIBUTION FROM THE PHARMACOLOGICAL RESEARCH LABORATORY, HYNSON, WESTCOTT AND DUNNING, AND THE PHYSICS RESEARCH LABORATORY, HANOVIA COMPANY]

EFFECT OF POLARIZED LIGHT ON THE PHARMACOLOGICAL PROPERTIES OF SOME DRUGS¹

BY DAVID I. MACHT AND W. T. ANDERSON, JR.

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Introduction

While the effect of light on chemical reactions has been known for a long time, and photochemistry has been receiving adequate attention for many years, the influence of light and other radiations on the pharmacological properties of drugs has not been studied until comparatively the last few years.

In the last decade or two, attention has been directed to the important role played by ultraviolet rays on the toxicity of a number of dyes, and very much more recently the effect of such radiations has come into prominence in connection with the marvelous strides in our knowledge of the vitamins. The earlier work on the dyes is summarized by Tappeiner and Jodelbauer² who have reviewed the previous work on the subject and contributed some original observations. These authors have found that eosin, while relatively non-toxic for paramecia in the dark, is very destructive to the same animalcules when irradiated by ultraviolet rays. Straub³ analyzed this photo-dynamic effect further and obtained some evidence pertaining to oxygen being activated in the course of this phenomenon. Noguchi⁴ and others have studied effects of light on the bactericidal properties of some dyes. Amsler and Pick⁵ and Kolm and Pick,⁶ studying the effects of eosin solutions on isolated organs, found that that compound was much more active when irradiated by ultraviolet rays than in the dark. Macht and Teagarden⁷ studied the effect of ultraviolet irradiations on the fluorescent solutions of quinine and quinidine sulfates and found that these solutions were more active when so irradiated. Recently Macht⁸ noted that the toxicity of sodium benzoate for yeast is much greater when exposed to sunlight than in the dark, and the remarkable experiments of Hess

¹ Read before a joint session of the Organic and Biological Divisions of the American Chemical Society at the Richmond meeting, April 12, 1927. A preliminary note on part of the subject was published by David I. Macht and J. C. Krantz, Jr. [*J. Am. Pharm. Assoc.*, 16, 106 (1927)].

² Tappeiner and Jodelbauer, *Ergebnisse Physiol.*, 8, 698 (1909).

³ Straub, *Arch. expil. Path. Pharmacol.*, 51, 583 (1904).

⁴ Noguchi, *J. Expil. Med.*, 8, 30 (1908).

⁵ Amsler and Pick, *Arch. expil. Path. Pharmacol.*, 82, 88 (1918).

⁶ Kolm and Pick, *ibid.*, 86, 1 (1920).

⁷ Macht and Teagarden, *J. Pharmacol.*, 22, 1 (1923).

⁸ Macht, *Proc. Soc. Expil. Biol. Med.*, 23, 638 (1926).

light the black diamond-shaped slit was substituted for the prism as described above.

Inasmuch as the authors have found, as will be shown further on, that irradiation, even with weak light, when polarized produces definite changes in drugs, another and slightly modified type of apparatus was employed in a different series of experiments. This set-up or arrangement was used in some of the most carefully and accurately performed experiments carried out by the authors, and consisted of the following. A wooden box with a detachable top is blackened inside and outside. Inside the box at one end is an attachment in which is fixed a rectangular quartz cell for the solutions of drugs. At the other end of the black box directly opposite the quartz cell is a circular aperture into which can be fitted snugly a Nicol prism, 2.5 cm. in diameter and 6 cm. long. In obtaining polarized light, the tube containing the Nicol prism is placed in the aperture so that its long axis is parallel to the table. In front of the Nicol prism is placed a small Spencer microscope lamp provided with a daylight filter. This lamp consists of a small Mazda lamp of 15 watts, enclosed in a dark cell with a window of glass which allows the light to diffuse through. The light from this lamp passing through the Nicol prism is polarized so that the drug contained in the quartz cell inside the black box is irradiated with polarized light. The amount of such polarized light and its intensity were very carefully determined by means of a thermopile. The exact wave lengths of which the light consisted were also determined by the spectrograph. In order to obtain a control light of exactly the same intensity and quality, with the exception of its not being polarized, the lamp is moved to a position from the aperture of the black box and the Nicol prism is removed. With the lamp in this position, and the Nicol prism taken out, the light entering the box is so calibrated as to be the exact control of the polarized light which was used. By means of this apparatus, which we may call for brevity the M.-A. (Macht-Anderson) apparatus, a drug can be radiated with polarized and non-polarized light for any given length of time so as to have the two forms of light of exactly the same intensity and wave length. Examples of experiments performed with the above apparatus will be given in the following section.

In order to obtain polarized light by the method of glass plates a different kind of apparatus was constructed. This apparatus was designed carefully by one of the authors and Professor A. H. Pfund, of the Department of Physics, Johns Hopkins University, and was constructed under Professor Pfund's supervision and calibrated by him. The plan of this apparatus is as follows. A box or cell in the form of a truncated pyramid 80 cm. high was constructed with a lower base 60×45 cm. and upper end about 25 cm. square, the back of the wall of the cell being perpendicular to the base, and the front wall and door slanting. At the upper

or small end of the cell a socket is fixed, into which is inserted a large, round, Mazda tungsten nitrogen electric bulb, of 500 watts power, which serves as source of light. The lower part of the apparatus or cell is divided into two compartments, completely separated from each other by a blackened partition. The light of the Mazda lamp is allowed to penetrate into the chamber on one side of the apparatus after first passing through a dozen plates of smooth glass, placed at the "polarizing" angle, so that this chamber is illuminated with highly polarized light. The light from the same Mazda lamp, on the other hand, is allowed to penetrate into the second or neighboring chamber after first passing through a pile of smooth plates of glass placed perpendicular to the line of propagation of the light, so that this second chamber is illuminated with non-polarized light. The number of glass plates in this second pile was adjusted so that the intensity of the non-polarized light was just equal to the intensity of the polarized light in the first chamber. By boring apertures in the floors of the two respective chambers and taking spectrophotographs of the two transmitted lights, it was found that the spectral range of light waves in the polarizing and non-polarizing chambers was the same, the shortest waves transmitted being about 3650 Å. The temperatures in the two chambers were practically the same, not deviating from each other by more than a fraction of a degree.

The source of light was an electric bulb of 700 candle power. This intensity, of course, was cut down by passage through the piles of plates, but the intensity of the transmitted light in each chamber was made the same by photometric calibration in the Physics Laboratory, performed by Professor A. H. Pfund. The intensities in the two chambers were compared by Professor Pfund by reflecting the lights passing through the two sets of glass plates, from a white surface, and allowing the rays to pass through a Lummer tube. The light from the two chambers was thus reflected diffusely, and hence was depolarized before the comparison was made. Thus, while the eye was used in comparing, it could not be argued that there might be a difference in the physiological effects of polarized and non-polarized lights on the eye. Of course such an objection would be purely hypothetical as, so far as is known, no difference in the effects on the eye between polarized and non-polarized lights has ever been noted, and if such a difference should be experimentally demonstrated, it would be a fundamental physiological discovery.

In order to make sure that small variations in intensity of the control did not affect the results, a number of experiments were made with the non-polarized light of a slightly greater or slightly lesser intensity than the polarized light (by changing the number of plates in the control chamber). Such variations did not appreciably change the marked effect of the polarized light.

The temperatures in the two chambers were the same to within a fraction of a degree, as indicated by thermometer readings and also by thermographic tracings. Here again a number of experiments were made in which the temperature in the control chamber was purposely made a little higher or a little lower than in the polarizing chamber, respectively, and the results obtained still showed a marked difference between the effects produced by polarized and non-polarized light.¹²

Methods of Pharmacological Evaluation

The drugs studied intensively in the present paper were a galenical preparation of tincture of digitalis and the pure crystalline drug cocaine, either in the form of the free base or of the hydrochloride. The hydrochloride of cocaine was used in most cases because of the very poor solubility of the alkaloid itself. In addition to these two drugs, the authors have studied also a number of others and more particularly quinine and cinchonidine. Extensive work is in progress on several important alkaloidal and other drugs, which will be reported in a later paper.

It is a well-known fact that physiological test objects are often so sensitive to the pharmacological effects of certain chemicals or drugs that by their means one can detect changes in those drugs much more easily than by any quantitative chemical methods. Indeed it is a fact that some of the most potent and important medicinal substances employed by pharmacologists and physicians can be standardized or assayed only by biological methods. Thus, for instance, the uterus of the virgin guinea pig will respond to such dilute concentrations of histamine as could not be quantitatively estimated by even the more refined microchemical methods and the very highly potent chemical body "A" obtained by Professor Abel¹³ from the posterior lobe of the pituitary gland, is some 40 or even more times more powerful in this respect, as shown by tests on the isolated uterus and on certain preparations of the urinary bladder.¹⁴

Digitalis, undoubtedly one of the most important and useful drugs in the Pharmacopeia, is a drug the chemistry of which is still but incompletely known, and the only methods by which the therapeutic efficiency or potency of digitalis preparations can be estimated and compared are biological. While cocaine is a well-known chemical entity and its chemical structure is very well understood, a dilute solution of it can be assayed chemically only with the greatest difficulty or almost not at all, and even then the results are not sufficient for determining its pharmacological activity. The same is true of the majority of alkaloidal drugs employed by pharmacologists and physicians, so that in order to evaluate various samples of

¹² Macht, *J. General Physiol.*, 10, 41 (1926).

¹³ Abel, Rouiller and Geiling, *J. Pharmacol.*, 22, 4, 289 (1923).

¹⁴ Macht, *J. Pharmacol.*, 27, 389 (1926).

the same drug biological or pharmacological methods of assay are quite indispensable and indeed are absolutely essential.

In the present work where the purpose of the irradiations was to detect even the smallest changes in the pharmacological properties of certain drugs, chemical methods could be employed only to a limited extent; the greatest amount of information had to be obtained and the greater reliance placed on pharmacodynamic tests and analyses.

Tincture of digitalis was used almost exclusively in the study of digitalis. The methods of assay employed in this case were of different kinds. In the first place the standard cat method of Hatcher and Brody was employed,¹⁵ the exact technique being a slight modification introduced by Rowntree and Macht.¹⁶ This method consists in the regular injection of tincture of digitalis diluted 1:10 with physiological saline solution into the femoral vein of a cat under light ether anesthesia. The injections are continued as described by the authors until the arrest of the heart in systole. An average of three experiments is usually made for an assay. The cat method has recently been shown by Lind Van Wijngarden, on the basis of a very large number of animal experiments, to yield quite reliable results in experienced hands.¹⁷ The figures from which averages were made lay well within the experimental variation allowed by the formula of Wijngarden, that is, the mean of the percentage deviations from the average value of the N estimations made was less than $6.67 \sqrt{N-1}$.

A still more sensitive and reliable method, especially for comparative examinations of different samples, has been described by one of the authors in collaboration with Krantz.¹⁸ In contradistinction to the cat method which is a zoöpharmacological method, this method is phytopharmacological, employing living seedlings or plants as the biological test objects. These two methods, the cat method and the plant method, were used almost exclusively by the authors in the study of tincture of digitalis. In addition to these a comparison of digitalis tinctures exposed to polarized and non-polarized light was also made by other methods. Thus, in some cases, the goldfish method of Pittenger and Vanderkleed was used.¹⁹ In still other experiments the comparative potency of the specimens treated with different forms of light was tested on frogs' hearts and finally some comparative tests were made by very interesting and effective methods described by Hanzlik and Shoemaker, in which the emetic effect of digitalis on pigeons is used as a criterion.²⁰ It may be stated at once that the results obtained by *all* of the above methods of experimenta-

¹⁵ Hatcher and Brody, *J. Am. Pharm.*, **82**, 360 (1910).

¹⁶ Rowntree and Macht, *J. Am. Med. Assocn.*, **66**, 870 (1916).

¹⁷ Van Wijngarden, C. de Lind, *Arch. expl. Path. Pharm.*, **12**, 252 (1926).

¹⁸ Macht and Krantz, *J. Am. Pharm. Assocn.*, **16**, 210 (1927).

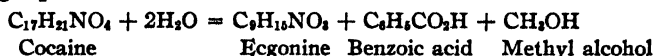
¹⁹ Pittenger and Vanderkleed, *ibid.*, **24**, 427 (1925).

²⁰ Hanzlik and Shoemaker, *Proc. Soc. Exptl. Biol. Med.*, **23**, 298 (1926).

tion with digitalis were quite concordant and in most cases at least two methods, namely, the cat and the plant methods, were used in examining each sample, so the results were doubly reliable.

The evaluation of cocaine in weak solutions, such as are generally employed in surgical practice and which are known to be easily decomposed by heat and other physical agents, is very difficult by chemical means, and moreover gives little information as to the therapeutic or pharmacological efficiency of the drug. In order to detect deterioration in cocaine solutions more effectively, two new and very delicate methods have been elaborated by one of the authors, one of these being a zoöpharmacological method and the other being phytopharmacological. In the *zoöpharmacological* method the effect of cocaine solutions was studied on goldfish, *Carassus aureus*. It was found that when fish are placed in even very dilute solutions of cocaine hydrochloride, for instance 1:10,000, they gradually become anesthetized and lose their sense of equilibrium. The fish "keel" over and finally float on their sides. A longer exposure leads to paralysis and death. To compare two specimens of cocaine, solutions are diluted to the same concentration in two vessels, small goldfish are immersed in the same and their behavior is studied. There is usually a preliminary stage of excitement which is followed by an anesthetic and a paralytic stage, and by noting the rapidity of onset of these phenomena it is easy to determine which solution is the more active pharmacologically. The more active solution in these cases is the one which produces anesthesia and paralysis more quickly.

The *phytopharmacological* method employed is even more delicate than the goldfish method. This method is based on the remarkable observations of Macht and Livingston obtained in a comparative study of the effects of cocaine on animal and plant protoplasm.²¹ It was found by those authors that whereas the cocaine molecule itself is not very toxic for living seedlings of *Lupinus albus*, requiring sometimes as much as 6% or more of the solution of cocaine hydrochloride to inhibit growth completely, and not affecting growth at all in concentrations of 0.17%, the decomposition products of the cocaine molecule behaved very differently. When the cocaine molecule is hydrolyzed or broken down it yields one molecule each of the base ecgonine, methyl alcohol and benzoic acid according to the following equation:



Of these decomposition products benzoic acid, when tested on animal preparations (in the form of sodium benzoate) is practically non-toxic, but when tested on plant preparations sodium benzoate is extremely toxic. It was found that as little as 0.0007 of 1% inhibited growth of *Lupinus*

²¹ Macht and Livingston, *J. General Physiol.*, 4, 573 (1922).

albus completely, and 0.004% produced an appreciable inhibition of growth of the roots. This method suggested a delicate means of determining the decomposition of cocaine solutions. The greater the decomposition, the greater the toxicity of the solutions becomes for the growth of living seedlings. In the present investigation this method yielded very striking results, as will be seen from Table I. In most of the experiments solutions of cocaine hydrochloride were used, but in some weak solutions of the alkaloid cocaine itself were also studied. Slight changes in the hydrogen-ion concentration of the solutions were found to produce no appreciable effect on the growth of the seedlings, so that the inhibition of growth was due actually to the decomposition products and more particularly to benzoic acid.

In addition to the above zoöpharmacological and phytopharmacological methods of evaluating cocaine solutions, samples of cocaine hydrochloride which were exposed to polarized and non-polarized light were also tested in other ways. The comparative *anesthetic* effect of the two solutions was studied on the cornea of the rabbit. The comparative anesthetic effect was also studied on the living frog skin. Finally, the anesthetic effect on human beings was studied on some subjects by direct application to the mucous membrane of the cheeks. The difference between solutions of cocaine exposed to polarized and non-polarized light was also tested by physical chemical methods, namely, the determination of their hydrogen-ion concentration. We are indebted to Mr. W. C. Harden for his kind assistance in this work.

In evaluating the potency of quinine and cinchonidine sulfates and other salts, the authors again made use of the phytopharmacological method. Several years ago one of the authors described the effect of solutions of cinchona alkaloids on the growth of plants and found that they were quite toxic for them.²² A comparative study of the toxicity of solutions of such alkaloids, therefore, was made by noting the growth of seedlings of *Lupinus albus* in definite percentage solutions of the drugs studied.

A few determinations were made also of the optical activity of quinine. In this case a quinine tartrate solution was employed which has been shown by Martinotti to be useful in the study of the keeping qualities of the drug, by means of observations on its optical rotation.²³

Experiments with Digitalis

Irradiation of digitalis tincture was performed by all of the methods described above. Tinctures of digitalis were taken and in each case a given specimen was divided into two parts. One of these was irradiated with

²² Macht, *Proc. Soc. Exptl. Biol. Med.*, 20, 1971 (1922).

²³ Martinotti and Martinotti, *Notiz. chim. ind.*, 1, 182 (1926).

polarized light; the other was irradiated with non-polarized light of the same intensity as a control. Occasionally the control with non-polarized light was irradiated with a stronger intensity of light or for a longer period of time. In all experiments the authors found that irradiation with polarized light produced a *change in the potency* of the tincture. Table I gives ample illustration of the findings.

In Expt. 101 irradiation was through a Nicol prism for one hour. The tincture of digitalis was in a glass test-tube, and the source of light was a Krohmayer lamp. In Expt. 106 irradiation was performed by the Macht-Pfund apparatus. The assay of the digitalis in these two experiments is given by the phytopharmacological method. Expts. 10 and 16 give the results obtained with irradiation by means of the Nicol prism and the Macht-Pfund apparatus, respectively, as indicated by assay experiments on cats. It will be noted that in each of these experiments irradiation with polarized light produced a deterioration of the tincture as indicated by a weaker pharmacological action of the same. It should be noted also that in all of these experiments the light employed consisted of rays belonging only to the visible spectrum plus some of the infra-red rays.

Expt. No. 200 was performed with the Macht-Anderson apparatus described above and in order to indicate the care exercised in controlling all the conditions in the experimentation, the physical data are here given in full. The apparatus used was the same as described above, the source of light being a microscope lamp with a daylight filter. The time of irradiation for each specimen, polarized and non-polarized, was exactly two hours. The radiation intensity for both polarized and non-polarized light was 70 ergs/sec./mm.² The light from the microscope lamp as determined by spectroscopic examination consisted of the visible rays and infra-red rays. All of the measurements were made with the greatest care by means of the thermopile. The average light intensity at the surface of the irradiated solution inside the blackened box was 5.538 ergs/sec./mm. the measurements in this case being made through water so that infra-red rays of more than 14,000 Å. were eliminated. The time of irradiation as stated above was two hours, or exactly 7200 seconds. The average light intensity measured here is the value obtained when the total intensity falling on the area is divided by area. This is necessitated by the fact that the light transmitted by the prism is not disposed uniformly. These very careful measurements established beyond a shadow of a doubt that any difference between the specimens obtained after irradiation must be due to polarization of the light because this was the only variable, the intensity, time of irradiation, the volume, surface and concentration of the drug irradiated being in all instances identical. It will be noted from the protocols of Expt. 200 that the assay of the polarized and non-polarized specimens by the cat method, by the plant method and by the pigeon

method all indicated that the polarized specimen was much more deteriorated than a non-polarized one.

Expt. 210 gives the results obtained by irradiation with the Krohmayer lamp. The tincture of digitalis here, as in previous experiments, was exposed in a quartz cell. In this case the rays transmitted were the visible rays with the exception of the extreme red and the ultraviolet rays ranging from 2500 to 4000 Å. In this experiment the polarized and non-polarized specimens were irradiated for 30 minutes each because the actual visible light intensity with this lamp was much higher than in the instance of the irradiation by the microscopic lamp. However, the intensity was lower because the microscope lamp produced an abundance of heat which was

TABLE I
TINCTURE DIGITALIS
Effect of a 0.5% soln. on growth of *Lupinus albus*

Expt. 101	Index of growth, %	Expt. 106	Index of growth, %
Original non-radiated tincture	54	Original non-radiated tincture	70
Irradiated through Nicol K. lamp, 1 hr.	69	Polarized in Macht-Pfund apparatus, 4 hrs.	84
Control, non-polarized	57	Control, non-polarized	71

1 10 assay on cats, average of three

Expt. 10	Lethal dose, cc./kg.	Expt. 16	Lethal dose cc./kg.
Original non-radiated tincture	9.2	Original non-radiated tincture	9.5
Irradiated through Nicol K. lamp, 1 hr.	13.0	Polarized in Macht-Pfund apparatus; temp. 26°	14.9
Control, non-polarized	10.0	Control, non-polarized, 6 hrs.; temp., 26°	12.6

Expt. 200, Macht-Anderson apparatus; exposure, 2 hrs.; 2 cm. Nicol; microscope lamp; visible and infra-red rays

Expt. 210, 3.5 cm. Nicol; Krohmayer lamp; 30 min; visible rays except red; ultraviolet, 2500-4000 Å.; Corning filter G986A

	Lethal dose for cats, cc./k		Growth of seedlings		Effect of 0.1 cc. on pigeons	
	Expt. 200	Expt. 210	Expt. 200	Expt. 210	Expt. 200	Expt. 210
Polarized	13.3	9.4	67	51	No vomiting in 20 min.	Vomits in 5 min.
Non-polarized	10.8	12.5	62	67	Vomits in 5 min.	No vomiting in 20 min.
Original, non-radiated	10.6	10.6	60	62	Vomits in 5 min.	

Expt. 30, May 14, 1926
Effect of soln. on cats;
average of three

Visible and
infra-red rays
Lethal dose,
cc./kg.

Expt. 40, June 15, 1926
Effect of soln. on growth
of *Lupinus albus*

	Lethal dose, cc./kg.	Index of growth, %
Polarized for 6 hrs	11.5	51
Non-polarized control	9.0	68
		52

Normal specimen
Specimen polarized for 6 hrs.
Non-polarizer control, 6 hrs.

not present from the light from the water-cooled Krohmayer lamp. The radiation density in this case, for both the polarized and non-polarized lights, was exactly the same, namely, 43 ergs/sec./mm.² The average light intensity at the surface of the irradiated source was in this case 42.66 ergs/sec./mm.² The intensity of this Krohmayer at the surface of the radiated specimen was 7.7 times that of the microscope lamp used above, while the time of irradiation with the Krohmayer was only one-fourth that used for the microscope lamp, or exactly 1800 seconds. Consequently, the samples irradiated by the Krohmayer rays received approximately twice as much light as those irradiated by the bulb. It was found that by irradiating digitalis tincture with ultraviolet light, a *further change or decomposition* in its constituents was produced. The tincture became actually more poisonous as indicated by the experiments on cats, pigeons and plants. Tincture of digitalis is a complex of a large number of active principles, the chemical nature of which is still not definitely known. It is, therefore, not at all surprising that progressive changes may be produced in it by irradiation with powerful rays for prolonged periods of time. The authors noticed in performing experiments on cats with such tinctures that the emetic properties of the tincture were markedly increased. This again indicated some change produced in the digitalis which is not ordinarily produced by the visible rays of light with which the other experiments were performed. *It is important to note, however, that here also it was the polarized light which produced a photodynamic effect, whereas the non-polarized control was relatively unaffected.*

Expts. 30 and 40 were performed with a Nicol prism and a Mazda nitrogen electric bulb of 75 watts.

Experiments with Cocaine

Table II exemplifies the effect of light on cocaine. In Expts. 120 and 50 the solutions were irradiated through a large Nicol prism. In Expts. 125 and 51 they were irradiated in the Macht-Pfund apparatus. It will be noted that in each case cocaine exposed to polarized light was markedly changed from the normal solution on the one hand and the one exposed to non-polarized light on the other hand. This was indicated by its lesser toxicity for animals (goldfish) and greater toxicity for seedlings, as explained above. Hydrogen-ion determinations also showed a change in the polarized specimens.

Expt. 220 shows the effect of polarized light of different wave lengths on solutions of cocaine hydrochloride. In this case irradiations with visible and infra-red rays were performed by the Macht-Anderson apparatus and microscope lamp under exactly the same physical conditions as described in the digitalis experiments. Irradiation with visible and ultraviolet rays was performed with the Krohmayer lamp with the same

physical constants as described under digitalis. Finally, ultraviolet rays alone were used in the third part of the experiment, by allowing the rays from the Krohmayer lamp to filter through a Corning filter G986A which allowed the rays from 2500-4000 Å. only to filter through. It will be noted in the case of cocaine that irradiations with polarized light of both short and long wave lengths produced a deterioration of the drug solution. This was tested out in every conceivable way; on living seedlings, on goldfish, on the rabbit's cornea, on the living frog's skin and on human mucosa.

TABLE II

	COCAINE		HYDROCHLORIDE		Time for paralysis of goldfish, min. (1:5000 soln.) ^f	
	PH		<i>Lupinus albus</i> , ^d index of growth, %			
	Expt. 120 ^a	Expt. 125 ^b	Expt. 120 ^a	Expt. 125 ^b	Expt. 120 ^a	Expt. 125 ^b
Original soln.	5.1	5.1 ^c	95 ^e	90		
Polarized specimen	4.9	4.9	82 ^e	80	16	No change after 25 min.
Non-polarized specimen	5.1	5.1	95 ^e	88	6	6

Growth of *Lupinus albus*, %

	Expt. 50 ^g	Expt. 51 ^h
Original soln.	105	100
Polarized specimen	91	75
Non-polarized specimen	106	100

Expt. 220

1:10,000 Soln. of cocaine hydrochloride

	Visible and infra-red rays, no ultraviolet, 2 hrs. Effect on plants, %	Visible and ultraviolet, no red or infra-red, 30 min. Effect on plants, %	Ultraviolet alone, 30 min. Effect on plants, %
Polarized	83	80	84
Non-polarized	98	95	93
Normal	100		

* A fresh solution of cocaine hydrochloride 1:1000 was made in distilled water. Twelve cc. of soln. was irradiated with a small Mazda electric bulb of 15 watts for 45 min. Another portion was irradiated with non-polarized light of the same intensity for 50 min.

^b Freshly prepared solutions of cocaine hydrochloride 1:1000 in distilled water. Two portions were irradiated for one hour in Macht-Pfund apparatus, one in polarized light, the other in non-polarized light of the same intensity, temperature of both being 26°.

^c 1:1000 solution.

^d The more cocaine decomposed, the greater the toxicity for plants.

^e 1:10,000 solution.

^f The more cocaine decomposed, the less the toxicity for animals.

^g December 5, 1925, irradiated one hour with Nicol prism.

^h December 8, 1925, irradiated three hours in Macht-Pfund apparatus.

In all three cases, the non-polarized specimens were more toxic on fish, and more anesthetic on rabbit's cornea, frog's skin and human mucosa.

Experiments with Quinine and Cinchonidine

In experiments with quinine and cinchonidine, solutions of quinine and cinchonidine sulfates, respectively, were used in most of the experiments. In some of the experiments a solution of quinine tartrate was examined. Irradiation of these solutions with polarized and non-polarized light of the visible spectrum by means of either a Nicol prism or the Macht-Pfund apparatus showed that such solutions became less toxic. This was easy to demonstrate quantitatively by means of phytopharmacological experiments. Expts. 60 and 70 will serve to illustrate the findings. In the case of quinine tartrate a few determinations with a polariscope were made which are indicated in Table III. Further polariscopic examinations are in progress.

TABLE III
PLANT TESTS, *Lupinus albus*

	Index of growth, %		Polariscope reading
	Expt. 70 ^{a,b}	Expt. 60 ^c	
Original soln.	77	56	—8°40'
Polarized specimen	87	72	—8°25'
Non-polarized specimen	77	64	—8°42'

^a October 7, 1926. Solutions of quinine tartrate 1%, especially prepared by Mr Fitzgerald Dunning. Two portions of this are irradiated for two hours in the two chambers of Macht-Pfund apparatus, at 26°; dilution, 1:100,000.

^b The more deterioration in quinine, the less the toxicity for plants.

^c January 20, 1926. Quinine sulfate irradiated for two hours in Macht-Pfund apparatus, 1 100,000 soln.

Experiments with Circularly-Polarized Light

In all of the above experiments with polarized light, *plane*-polarized light was obtained. The question naturally arises, what may be the effect of circularly-polarized light on the pharmacological properties of the above drugs? Such an investigation is at present in progress. It may be well, however, to state the results of a few preliminary experiments on the subject. The authors obtained circularly-polarized light by the use of the Macht-Anderson apparatus together with certain quartz plates. It has been found by physicists that if a ray of light passes through a plate of crystal quartz which has been cut perpendicularly to the axis, it is divided into two rays moving with different velocities, the vibrations in each ray, however, instead of being rectilinear and at right angles to one another, like plane-polarized light, are circular and in opposite directions. The ray of light is said to be circularly polarized. Ordinary complex light passing through such a plate will be circularly polarized, but the net result will be little, if any, different from that of the ordinary rays which were already vibrating in all directions. If the ray of light which passes through the quartz plate be already plane-polarized, for example, by means of a Nicol prism, the two beams emitted by the quartz plate will be circularly

polarized. Experiments were, therefore, performed by taking a quartz plate cut perpendicular to the axis of the crystal and allowing the plane-polarized light obtained by passing light from a microscope lamp through the Nicol prism to pass through this plate. Control experiments for the same were made by allowing the plane-polarized light to pass through another quartz plate cut parallel to the axis of the crystal. Table IV will give an idea of the results obtained with tincture of digitalis. The experiments indicate that circularly-polarized light produced even greater deterioration of the tincture than did the plane-polarized light. Further work on the subject is to be carried on.

TABLE IV
TINCTURE DIGITALIS

Macht-Anderson apparatus; 2cm. Nicol; microscope lamp; visible and infra red rays; exposure, 2 hrs.

Irradiated by	Lethal dose for cats, cc./kg.	Effect on seedlings, index of growth, %	Effect of 0.15 cc. on pigeons, vomiting in
(Normal, non-radiated)	11.2	59	3 min.
Non-polarized light	11.4	63	3 min.
Plane-polarized light	13.1	68	4 min.
Circularly-polarized light	15.1	73	6 min.

The authors are also planning to study the effects of polarized and non-polarized monochromatic lights.

Discussion

The experiments described above make it evident that polarized light may produce a profound change in the pharmacological properties of certain drugs. Perhaps the most remarkable fact in this connection is that such changes *are produced by polarized light of the ordinary or visible spectrum*. This is not only of scientific interest but of practical importance, as may be concluded from the following considerations. Polarized light is not at all as rare or uncommon as might be supposed on first thought. Wherever light is reflected from smooth surfaces some polarization occurs. Again, whenever light passes through certain transparent media such as glass at certain angles a little polarization takes place. It is known to physicists and physical chemists that transparent sheets of cellulose polarize light to a certain extent. In other words, thin sheets of paper which are more or less transparent produce considerable polarization of light that passes through them. Bearing this in mind the authors performed the following experiment. A tincture of digitalis was divided into two parts and corked tightly in two flint glass bottles of exactly the same shape and quality. One of the bottles was wrapped in thin tissue paper such as is often used by drug manufacturers for wrapping various vials of medicaments. The two bottles were left standing in the sunlight for several weeks and then the tinctures were assayed carefully both by the

plant method and by the cat method. It was found that while the quantity of light, as determined by physical measurements, that passed through the paper into the wrapped specimen of digitalis was less than one-sixth the quantity of light which passed through the uncovered glass bottle, nevertheless, the deterioration of the digitalis specimen in the paper-covered specimen was actually *greater* than in the uncovered specimen. Thus the index of growth for plant seedlings of *Lupinus albus* given by the uncovered specimen was 66%, whereas the index given by the paper-covered specimen was 71%. The lethal dose for cats of the uncovered specimen, was 9.2 cc. per kg., whereas the lethal dose of the paper-covered specimen was 10.6 cc. per kg., a difference of nearly 15%. Bearing in mind that the amount of light to which the covered specimen was exposed was less than one-sixth that of the uncovered specimen, these findings are truly remarkable. Similar results were obtained by exposing specimens of digitalis in test-tubes wrapped in thin tissue paper to the light from a large electric bulb. As another example of the practical importance of polarized light we may quote from a recent article on some interesting studies concerning the follicular hormone of the ovary, by Jordan and Doisy,²⁴ in the Proceedings of the Society of Experimental Biology and Medicine, December, 1926. We read, "In an earlier publication Allen and Ellis call attention to the destruction of the hormone by ultraviolet light. Some data, which confirm and extend theirs, have been obtained, but our most striking observations are upon the effect of diffuse daylight from north windows upon the activity of the hormone." To the present authors these findings have undoubtedly a significance in relation to polarized light, as may be made clearer by another citation. We quote from the pioneer work of Baly and Semmens on the hydrolysis of starch,²⁵ "In this connection it is interesting to note that in the living leaf the starch synthesized during the day undergoes hydrolysis to sugars in the early evening when, as is well known, the light from the sky is polarized. The results obtained would seem to show that plane-polarized light exerts very definitely a selective photochemical effect compared with ordinary light." Again, on page 253, we read "These experiments have been repeated more than twenty times and similar results were obtained in all. In the early observations some hydrolysis was sometimes observed on the slide exposed to ordinary light, and this effect varied in a remarkable way. It was found, however, that this was due to stray light reflected from the bench top and from the legs of the microscope stand, and also from the glass slide, and hence partially polarized. When this stray light was excluded, the abnormal effect vanished and constant results were obtained."

In the opinion of the authors the above phenomena can be explained

²⁴ Jordan and Doisy, *Proc. Soc. Exptl. Biol. Med.*, **24**, 216 (1926).

²⁵ Baly and Semmens, *Proc. Roy. Soc.*, **97B**, 280 (1924).

satisfactorily on the basis of the photochemical and the photopharmacological effects of polarized light.

While the phenomena and experiments just described are rather unusual, on more careful reflection they do not seem to be as unexpected as one might be inclined to regard them. They are no more striking than the fact that solutions of organic chemicals possessing an asymmetric carbon atom have the power of turning the plane of polarized light to the right or to the left. If "for every action there is a reaction" we may look at this phenomenon from the other end and argue that if a given solution can turn the plane of polarized light to the right or to the left, then *vice versa* we may expect polarized light also to react on the solution, and tend to produce some rearrangement of its molecules. This is, however, only by way of speculation. The authors may state in this place that they are continuing further work on the effects of polarized light on a considerable number of other drugs and have already sufficient evidence to indicate that many such drugs are changed in their pharmacological properties by such light. Furthermore, it may be stated in this place, it was interesting to find that wherever such a change in the pharmacological properties was produced by polarized light, an inquiry into the chemical structure of the drugs studied, so far as is known, revealed that they were optically active. These results which are not final but require further study make it evident that optical activity of various chemical compounds is of even greater importance than has hitherto been supposed. We may conclude with a quotation from an article by the late Professor Arthur R. Cushny on the biological relations of optically isomeric substances, "This optical activity is, in fact, the most persistent evidence of life which we possess. An optically active alkaloid or acid may be kept for centuries after the plant which formed it and the chemist who isolated it are dead, but it will still possess its optical activity, testifying that it was formed by some living thing either directly or indirectly. When we find an optically active substance in the earth, we may know at once that it arose through the agency of life. The petroleum we burn, for example, must have arisen from living tissues, for it is optically active. Not only is it the most persistent sign of life, but it is the most definite physical characteristic of life. No other can be measured in actual numbers in the same way."

Summary

1. The effect of polarized light of different wave lengths was studied on a number of drugs and more particularly on tincture of digitalis solutions of cocaine and its salts, and quinine.
2. Polarized light was obtained by the two classical methods: (A) with a Nicol prism, (B) by means of piles of glass plates.
3. Controls were carefully performed with non-polarized light of exactly

the same physical properties and with the same physical constants except as to polarization.

4. It was found that polarized light beyond any doubt produced a very definite change in the pharmacological properties of the drugs studied as compared both with the normal specimens and with specimens irradiated by non-polarized light.

5. The practical significance of the above observations is discussed.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE U. G. I. CONTRACTING COMPANY]

THE SHIFT IN A NEAR INFRA-RED ABSORPTION BAND OF SOME BENZENE DERIVATIVES

BY JAMES BARNES AND W. H. FULWEILER

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In connection with a search for possible spectroscopic methods of identifying hydrocarbons some work was done on the absorption spectra of the aromatic series. Aside from the practical aspects of the results obtained it was thought that a preliminary report of some of the data might be of theoretical interest to those who are working in this field.

The extensive investigations of Coblenz¹ and Puccianti² on infra-red absorption spectra of organic liquids gave many important results. In recent years, certain special fields have been studied in a more detailed manner. We refer to the works of Márton,³ Ellis⁴ and others who showed that there appeared in the absorption spectra of the carbon-hydrogen compounds which they investigated a series of bands all at approximately the same wave length and that the values of these wave lengths almost formed an harmonic series, the fundamental being near 6.5μ .

Apparatus and Methods

All the above-mentioned observers used a prism spectroscope with a radiometer or a thermopile as the detecting instrument. In our work on the absorption spectra of some hydrocarbons and petroleum oils we have been using a grating spectroscope and photographing the bands on plates sensitized with neocyanine.

The source of radiation was a 65-watt lamp with a short, straight filament. It was surrounded by a hood with a hole in its side. The light passing through this hole fell on a lens which rendered it approximately parallel. It then passed through the absorption cell to another lens which

¹ Coblenz, *Carnegie Inst. Pub.*, 1905-8.

² Puccianti, *Nuovo Cim.*, 11, 241 (1900).

³ Márton, *Z. physik. Chem.*, 117, 97 (1925).

⁴ Ellis, *Phys. Rev.*, 27, 298 (1926).

focused the light on the slit of the spectroscope. By means of screens with circular openings placed before and after the cell, only the light passing through the cell fell on the slit. The absorption cells were made from glass tubing 2 cm. in diameter with plane glass windows glued to ground ends and with side tubes for filling. Two lengths of cells were used, 18 and 30 cm., respectively.

A Rowland plane reflection grating was placed on the table of the spectrometer and carefully adjusted. The collimator and camera objectives had apertures of 3.5 cm. and their focal length was approximately 40 cm. Photographs were only taken in the first order spectrum and all lines of the second order which would affect the plates in the region under investigation were absorbed by a thin sheet of red glass placed in front of the slit. The photographs were taken by exposing one-half of the slit to the light after passing through the absorption cell, and the other half to the light from copper and nickel arcs.

Meggers⁵ values for the wave length of the copper lines and Meggers and Kiess⁶ values of the nickel lines in the near infra-red region were taken as standards for measurement. The dispersion of the spectroscope as used was approximately 39.8 Å. per millimeter. Measurements of the plates were made in the usual manner on a comparator reading to 0.001 mm.

Discussion of Results

The results given in Table I are the means of many measurements made upon the center of the absorption bands photographed on two plates for each substance, one with the longer and the other with the shorter cell. The results are believed to be accurate to within ± 5 Å.

Table I gives the wave lengths in Å. units and the wave numbers ($1/\lambda$) in cm.^{-1} reduced to vacuum as obtained from Kayser's "Tabelle der Schwingungszahlen."

TABLE I

WAVE LENGTHS AND WAVE NUMBERS OF ABSORPTION BANDS OF BENZENE DERIVATIVES

	λ (Å)	$1/\lambda$ (cm.^{-1})		λ (Å)	$1/\lambda$ (cm.^{-1})
Benzene	8741	11437	<i>m</i> -Xylene	8793	11370
Toluene	8758	11415	<i>p</i> -Xylene	8808	11350
Ethylbenzene	8772	11397	Diethylbenzene ^a	8799	11362
<i>o</i> -Xylene	8781	11385	Mesitylene	8844	11304

^a Mixture of *m*- and *p*-diethylbenzene.

Table I shows that there is a progressive shift of the absorption bands toward the longer wave lengths and hence a decrease in the frequencies with the addition of methyl and ethyl groups to the benzene ring.

Table II shows the frequencies ($\nu \times 10^{-11}$) and the difference produced by quantum addition of ethyl and methyl groups, respectively.

⁵ Meggers, *Bur. of Standards, Bull.*, 14, 385 (1918-19).

⁶ Meggers and Kiess, *ibid.*, 14, 649 (1918-19).

TABLE II
FREQUENCIES OF ABSORPTION BANDS AND THEIR DIFFERENCES

	Benzene	Ethyl- benzene	Diethyl benzene	Toluene	Xylene ^a	Mesitylene
Frequency $\times 10^{11}$	3431	3419	3409	3424	3410	3391
Difference	...	12	10	7	14	19

^a Mean of xylenes.

Table III shows that the frequency depends on the position of the methyl groups in the xylenes.

TABLE III
FREQUENCIES OF THE ABSORPTION BANDS OF THE XYLENES AND THEIR DIFFERENCES

Xylene	<i>o</i>	<i>m</i>	<i>p</i>
$\nu \times 10^{11}$	3415	3411	3405
Diff.	...	4	6

While there is probably no justification for extending the Bjerrum-Schwarzschild theory of band spectra to liquids, yet it is of some interest to note that, with the resolving power employed, no doubling of the bands nor any sign of fine structure was observed on any of the photographic plates.

The effect of the addition of methyl or ethyl groups on the molecular forces of the benzene ring is not well understood. However, if the effect is small compared to the effect of the added mass one would expect on a theory such, for example, as that proposed by Debye that the change in the frequency would be inversely proportional to some function of the added mass. The results above are at least in qualitative agreement with such a theory.

In this connection the following data given by Ellis⁷ are of interest.

DISPLACEMENT OF A 14μ BAND IN THE SPECTRA OF THE BENZENE DERIVATIVES

Benzene	Toluene	<i>o</i> -	-Xylene- <i>m</i> -	<i>p</i> -	Mesitylene
14.1	13.85	13.55	12.95	12.55	11.95

These results taken from Coblenz' curves show that in these bands which Ellis attributes to the carbon-carbon bond, the wave lengths shift progressively toward the shorter wave lengths as methyl groups are added, which is in the opposite direction to the results recorded above.

In conclusion, we wish also to report that plates were taken of the absorption spectrum of benzene produced by a cell of 80 cm. length. No absorption was found at wave lengths 0.835μ and 0.760μ , but a band clearly appeared at 7134 \AA . With this length of cell the band at 7134 \AA . is easily observed visually.

Summary

By means of a grating and plates sensitized with neocyanine, absorption bands of benzene and of some of its derivatives have been photographed

⁷ Ref. 4, p. 313.

and their wave lengths measured. The results show a progressive shift of the bands toward lower frequencies as methyl and ethyl groups are added. There is also a shift due to the position of the methyl group in the xylenes.

With a cell 80 cm. in length, benzene shows an absorption band at 7134 Å.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE, No. 132]

THE CHEMISTRY OF LIGNIN. I. LIGNIN FROM CORN COBS

By MAX PHILLIPS

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In spite of the extensive literature on lignin the chemistry of this product remains obscure.¹ Nothing definite is known about its constitution, although various formulas have been proposed, among which may be mentioned that of Cross and Bevan² for lignin ("lignone") from jute, and those of Green,³ Klason⁴ and Schrauth.⁵ Most of these formulas have little definite chemical evidence in their support. That of Schrauth is admittedly speculative, although this investigator has endeavored, with some success, to correlate the conflicting data on lignin found scattered in the literature. The difficulty in deducing a constitutional formula for lignin is primarily due to the fact that as yet no method has been developed for the isolation of lignin in the pure state, nor is there any method known by which its purity may be gaged. The usual criteria of purity cannot, of course, be applied. The problem as to whether lignin is a homogeneous substance or a mixture of closely related chemical substances, therefore, remains unsolved. This has been further complicated by the fact that various investigators have obtained their lignin from different sources and by different methods. It has been obtained from (1) sulfite or soda and sulfate liquors resulting from the preparation of paper pulp from wood, (2) wood treated with 64-72% of sulfuric acid, (3) wood or similar lignin-containing plant material treated with saturated

¹ An extensive review of the literature is found in a recent monograph by Walter Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926. Hawley and Wise, in their monograph on "The Chemistry of Wood," The Chemical Catalog Co., New York, 1926, give a critical review of our present knowledge of the chemistry of lignin, particularly that obtained from wood. An excellent résumé of the literature is given in a paper by Zhereboff [*Paper Trade J.*, **86**, No. 27, 47 (1925)].

² Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2nd ed., 1895, p. 137; Vol. III, 1912, p. 104.

³ Green, *Z. Farben Textilchemie*, **3**, 97 (1904).

⁴ Klason, *Ber.*, **56**, 300 (1923).

⁵ Schrauth, *Z. angew. Chem.*, **36**, 149 (1923).

hydrochloric acid (so-called Willstätter lignin),⁶ (4) lignin-containing substance digested with 10% of sodium hydroxide solution at 130° (Powell and Whittaker),⁷ or with 1.5% of aqueous or 2% of alcoholic sodium hydroxide solution at room temperature (Beckmann, Liesche and Lehmann).⁸

The lignin fraction described in this paper was prepared by the alcoholic sodium hydroxide method of Beckmann, Liesche and Lehmann, as this treatment was considered least likely to bring about any drastic changes in its composition. It would hardly be expected that the lignin obtained by the hydrochloric or sulfuric acid methods, or from the sulfite or soda and sulfate liquors, would be identical with that which occurs in the plant substance. That these drastic treatments do bring about marked changes in the composition of the lignin has been pointed out by a number of investigators.^{5,9} On the other hand, the lignin obtained from flax shoves by the method of Powell and Whittaker and from winter rye straw by that of Beckmann, Liesche and Lehmann appears to have been a fairly homogeneous substance. The results obtained in this investigation agree closely with those of Beckmann, Liesche and Lehmann and of Powell and Whittaker. Recognizing that in the absence of any criteria of purity all data must be interpreted with considerable caution, the results obtained, nevertheless, warrant the conclusion that the lignin fraction from corn cobs is a fairly homogeneous substance or a mixture of closely related isomers. The fact that the results on lignin from corn cobs agree fairly closely with those of Powell and Whittaker, who used a somewhat different method for obtaining the lignin from flax shoves, is certainly noteworthy. All the data obtained agree fairly closely with the formula $C_{40}H_{46}O_{16}$ for lignin from corn cobs. (The formula given by Beckmann, Liesche and Lehmann for lignin from winter rye straw is $C_{40}H_{44}O_{16}$, and that of Powell and Whittaker for lignin from flax shoves, $C_{45}H_{48}O_{16}$.) It contains three methoxyl groups and at least four hydroxyl groups. No carboxyl groups are present. The acidity is due to phenolic hydroxyl groups.

There has been a great deal of discussion¹⁰ on the question of whether pentosans or furfural-yielding bodies may be considered as part of the structural arrangement of the lignin molecule or as an impurity associated with lignin. The lignin fraction obtained from corn cobs, even after prolonged distillation with 12% hydrochloric acid, gave no test for furfural

⁶ Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

⁷ (a) Powell and Whittaker, *J. Chem. Soc.*, **125**, 357 (1924); (b) **127**, 132 (1925).

⁸ Beckmann, Liesche and Lehmann, *Z. angew. Chem.*, **34**, 285 (1921).

⁹ Schwalbe, "Die Chemie der Cellulose," Gebrüder Borntraeger, Berlin, 1911, p. 421. Hönig and Spitzer, *Monatsh.*, **39**, 1 (1918). Lange, *Z. physiol. Chem.*, **14**, 15, 217 (1890). Rinman, *Papier Ztg.*, **35**, 221 (1910).

¹⁰ Hägglund, *Ber.*, **56**, 1866 (1923). Heuser, *Cellulosechemie*, **4**, 77 (1923). Hägglund and Malm, *ibid.*, **4**, 73, 85 (1923).

in the distillate. The absence of pentosans or furfural-yielding bodies in the lignin fraction from corn cobs must then be assumed.

Experimental Part

Isolation of Lignin.—One thousand g. of corn cobs, cut in small pieces, was treated with 4 liters of 2% alcoholic sodium hydroxide solution (made by dissolving 80 g. of sodium hydroxide in 1600 cc. of water and making this up to a volume of 4 liters with 95% ethanol) and allowed to stand at room temperature for three days. The yellow alcoholic solution was decanted off, the cobs were pressed out, and the liquid was added to the solution obtained by decantation. This was filtered, neutralized with hydrochloric acid and concentrated by distilling on the water-bath under reduced pressure. Hydrochloric acid was added to the concentrated liquid, whereupon the lignin separated as a light yellow gum. This was filtered off, washed free from acid, and dried at 80° under reduced pressure. The yield was 3.49% of the weight of cobs taken. The lignin was a light yellow, amorphous powder. It reduced Fehling's solution. A portion of the lignin obtained as described above was redissolved in cold, dil. sodium hydroxide solution and then reprecipitated with hydrochloric acid. A carbon and hydrogen determination made on this fraction and upon the original batch showed no material change in composition. Two typical analyses are given below:

Anal. Subs., 0.2070, 0.2065; CO₂, 0.4637, 0.4638; H₂O, 0.1095, 0.1080. Found: C, 61.08, 61.24; H, 5.91, 5.85.

A molecular-weight determination made upon the substance by the boiling-point method, using glacial acetic acid as the solvent, gave the following results.

Mol. Wt. Subs., 0.3787, 0.3633, 0.3445; solvent, W, 24.1160, 24.2970, 24.3570; Δt , 0.065, 0.060, 0.060. Found: M, 753, 777, 735; mean, 755.

From a consideration of all the data, the formula C₄₀H₄₆O₁₆ has been assigned as the most probable one for this lignin fraction from corn cobs. The molecular weight and the percentage composition calculated for a compound of this formula are: M, 782.5; C, 61.36; H, 5.92; O, 32.72.

A methoxyl determination made on the lignin using the Zeisl and Fanto¹¹ method gave the following results.

Methoxyl. Subs., 0.3000, 0.3000, 0.3000, 0.3000; AgI, 0.2766, 0.2800, 0.2712, 0.2705. Calcd. for C₄₁H₄₇O₁₅(OCH₃)₁: CH₃O, 11.9. Found: 12.1, 12.3, 11.9, 11.9.

A 2g. sample of the lignin was distilled with 12% hydrochloric acid, following the A. O. A. C. method¹² for the determination of pentosans. The distillate gave a negative test for furfural with aniline acetate test paper and no precipitate with the phloroglucinol reagent.

Acetylation of Lignin.—The acetylation of the lignin was carried out, following the method of Powell and Whittaker.^{7a} Ten g. of lignin was treated with 20 cc. of acetic anhydride, a few drops of concd. sulfuric acid were added, and the mixture was heated on the steam-bath for one hour. After cooling, it was poured into ice water, and the precipitate filtered off, and washed with cold water until the washings were free from acid. The product was dried over sulfuric acid in a vacuum desiccator. It was obtained as a brown, amorphous powder, insoluble in cold, dil. alkali, indicating that the

¹¹ Houben, "Die Methoden der Organischen Chemie," Vol. III, Georg Thieme, Leipzig, 1923, p. 144.

¹² "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Association of Official Agricultural Chemists, Washington, D. C., 1925.

acidity of the lignin is due to phenolic hydroxyl groups. The acetyl determination was made following the method of Perkin.¹⁸

Acetyl. Subs., 1.0000, 1.0000, required 8.06 cc., 8.08 cc. of 0.5*N* KOH. Subs., 0.3000, 0.3000; AgI, 0.2377, 0.2370. Calcd. for $C_{47}H_{38}O_{13}(CO_2CH_3)_4(OCH_3)_3$: CH_3CO , 18.1; CH_3O , 9.8. Found: CH_3CO , 17.3, 17.4; CH_3O , 10.4.

Chlorination of Lignin.—The directions given by Powell and Whittaker^{7a} for the chlorination of lignin were followed. Ten g. of lignin was suspended in 80 cc. of carbon tetrachloride, and a slow stream of dry chlorine gas was passed in until no more hydrogen chloride was given off from the reaction mixture. The product was filtered off and dissolved in concentrated acetone solution (two volumes of acetone and one volume of water). The chlorolignin was precipitated by pouring the solution into dil. hydrochloric acid. It was filtered off, washed free from acid and dried over sulfuric acid in a vacuum desiccator.

Anal. Subs., 0.3072, 0.2214, 0.2235; AgCl, 0.3985, 0.2880, 0.2903. Calcd. for $C_{46}H_{36}O_{13}Cl_{10}$: Cl, 31.45. Found: Cl, 32.09, 32.17, 32.13.

Summary

The results of a chemical study of a lignin fraction from corn cobs indicate that the lignin is a fairly homogeneous substance or a mixture of closely related isomers. All the results agree closely with the formula $C_{40}H_{46}O_{16}$ for lignin from this source. The presence of four hydroxyl groups capable of being acetylated and of three methoxyl groups has been shown.

The results obtained on lignin from corn cobs are in close agreement with those obtained by Beckmann, Liesche and Lehmann on lignin from winter rye straw and with the results of Powell and Whittaker on lignin from flax shoves.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

ALICYCLIC DERIVATIVES OF RESORCINOL

BY RALPH H. TALBOT¹ WITH ROGER ADAMS

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The search for a superior substance which will exert a bactericidal activity against the organisms of the urinary tract has led recently to the discovery of *n*-hexyl-resorcinol by Dohme, Cox and Miller.² Although this substance has proved disappointing in its clinical results as compared with expectations drawn from preliminary work,³ nevertheless it presents an interesting field of bactericidal compounds.

The original investigators prepared various types of alkyl resorcinols,

¹⁸ Perkin, *Proc. Chem. Soc.*, 20, 171 (1904).

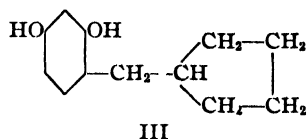
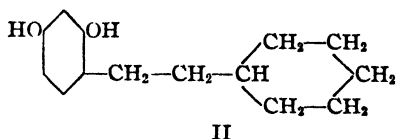
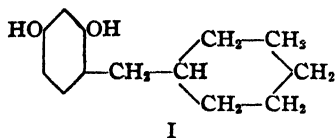
¹ This communication is an abstract of a portion of a thesis submitted by Ralph H. Talbot in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Dohme, Cox and Miller, *THIS JOURNAL*, 48, 1688 (1926).

³ Leonard, *J. Am. Med. Assoc.*, 83, 2005 (1924).

and found *n*-hexyl-resorcinol to be the most effective. Klarmann⁴ has extended the field to benzyl- and β -phenylethyl-resorcinols and to certain dialkyl-resorcinols, but these compounds possess lower phenol coefficients than hexyl-resorcinol. Twiss⁵ has described caproyl-resorcinol.

This investigation has had as its object the preparation of certain alicyclic derivatives of resorcinol, in particular hexahydrobenzyl-resorcinol (I), β -cyclohexylethyl-resorcinol (II), and cyclopentylmethyl-resorcinol (III).



These compounds were deemed worthy of study because of the fact that the presence of an alicyclic grouping in compounds prepared in connection with another field of work caused a marked increase in bactericidal action of a certain type as compared with the corresponding open-chain compounds.

The method of preparation was similar to that previously used for this type of compound, namely, the condensation of hexahydrobenzoic acid, cyclopentane-carboxylic acid and cyclohexyl-acetic acid with resorcinol in the presence of zinc chloride to obtain the corresponding ketones. The ketones were then reduced by the method of Clemmensen in order to convert the ketone carbonyl to a methylene group.

The three new resorcinol derivatives all have a high phenol coefficient but lower than that of *n*-hexyl-resorcinol.

Experimental Part

The procedure for preparing the ketones and the reduction of the ketones was exactly the same as that described by Dohme, Cox and Miller.²

Cyclohexyl-acetic acid was prepared as described by Hiers and Adams.⁶

Cyclopentane-carboxylic acid was prepared by the action of carbon dioxide on cyclopentylmagnesium bromide, followed by hydrolysis. The preparation of the Grignard, the addition of the carbon dioxide and the hydrolysis were carried out in accordance with the general procedure for

⁴ Klarmann, *THIS JOURNAL*, **48**, 791, 2358 (1926).

⁵ Twiss, *ibid.*, **48**, 2206 (1926).

⁶ Hiers with Adams, *ibid.*, **48**, 2385 (1926).

forming acids from Grignard reagents as described by Gilman and Parker.⁷ From 278 g. of cyclopentyl bromide, 120 g. (56%) of cyclopentane-carboxylic acid was obtained.

TABLE I

KETONES

	M. p., °C.	Solvent	B. p., °C. (4 mm.)	Yield, %	Subs., g.	Analysis H ₂ O g.	CO ₂ g.	Calcd., % C	% H	Found, % C	% H
1. Cyclohexyl-resorcylic ketone	115.5-116	Chloroform and petroleum ether	200-202	54	0.1497	0.0977	0.3894	70.86	7.32	70.93	7.30
2. Cyclohexyl-methyl-resorcylic ketone	111-112	Chloroform and petroleum ether	202-204	47	.1536	.1041	.4020	71.75	7.74	71.36	7.58
3. Cyclopentyl-resorcylic ketone	...		184-190	34							

TABLE II

ALICYCLIC RESORCINOLS

	M. p., °C.	Solvent	Yield, %	Subs., g.	Analysis H ₂ O g.	CO ₂ g.	Calcd., % C	% H	Found, % C	% H
1. Hexahydrobenzyl-resorcinol	116.5-117.5	Chloroform	55.6	0.1615	0.1274	0.4485	75.67	8.80	75.73	8.83
2. β -Cyclohexylethyl-resorcinol	109-110	Chloroform and petroleum ether	65	.1528	.1238	.4261	76.13	9.15	76.04	9.06
3. Cyclopentyl-methyl-resorcinol	95-96	Chloroform and petroleum ether	small	.1500	.1130	.4090	74.95	8.39	74.33	8.42

Summary

Hexahydrobenzyl-resorcinol, β -cyclohexylethyl-resorcinol and cyclopentylmethyl-resorcinol have been prepared. Their phenol coefficients are less than that of *n*-hexyl-resorcinol.

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⁷ Gilman and Parker, "Organic Syntheses," John Wiley and Sons, New York, Vol. V, 1925, p. 75.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

POLYHYDROXY-METHYLANTHRAQUINONES.

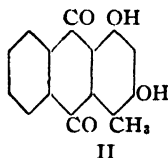
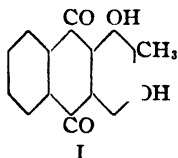
IX. CONTRIBUTION TO THE STRUCTURE OF RUBIADIN

BY FLORENCE D. STOUDER¹ WITH ROGER ADAMS

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Rubiadin is one of the pigments of madder² in which it occurs as a glucoside. Its monomethyl ether has been isolated from *morinda longiflora*^{3a} and *morinda citrifolia*.^{3b} Rubiadin was first isolated by Schunck and Marchlewski⁴ who, after analysis and molecular-weight determinations, assigned to it the composition of a dihydroxy-methylantraquinone. By oxidation it yielded phthalic acid thus indicating that all of the groups present were in the same ring. There are thus six possible isomers, 1,2-dihydroxy-3-methyl-, 1,2-dihydroxy-4-methyl-, 1,4-dihydroxy-2-methyl-, 2,3-dihydroxy-1-methyl-, 1,3-dihydroxy-2-methyl- and 1,3-dihydroxy-4-methylantraquinone. The first three are known substances and do not resemble rubiadin; the fourth is not known, but with two adjacent hydroxyl groups it should have reactions similar to those of alizarin and hystazarin, reactions which it does not possess. Rubiadin has, therefore, very probably either the fifth (I) or sixth (II) formula, and is a purpuroxanthin derivative as is indicated also from its color reactions—red with alkali and yellow with concd. sulfuric acid.



Schunck and Marchlewski synthesized the 1,3-dihydroxy-2-methylantraquinone and showed that it resembled rubiadin very closely in its color reactions and had the same melting point, 290°. The diacetate of rubiadin, however, melted at 225°, and that of the synthetic product at 217°. As a consequence these investigators assumed rubiadin to be the 1,3-dihydroxy-4-methylantraquinone.

The monomethyl ether of rubiadin (m. p., 290°), as isolated by Barrowcliff and Tutin from *morinda longiflora*, formed on demethylation a dihydroxy-methylantraquinone (m. p., 290°), whose diacetate melted

¹ This communication is an abstract of a portion of a thesis submitted by Florence D. Stouder in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School at the University of Illinois.

² Perkins and Everest, "Natural Organic Coloring Matters," Longmans, Green and Co., London, 1918.

³ (a) Barrowcliff and Tutin, *J. Chem. Soc.*, 91, 1909 (1907). (b) Simonsen, *ibid.*, 117, 561 (1920).

⁴ Schunck and Marchlewski, *ibid.*, 63, 969, 1137 (1892); 65, 182 (1894).

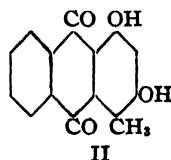
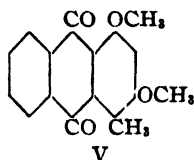
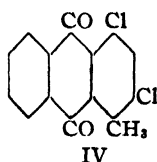
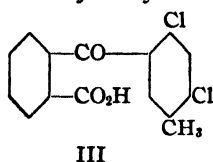
at 225°. Although these are the melting points of rubiadin and its derivative, these investigators assigned to the compound the structure of the monomethyl ether of 1,3-dihydroxy-2-methylantraquinone, in spite of Schunck and Marchlewski's conclusions.

In this investigation the 1,3-dihydroxy-4-methylantraquinone (II) and its derivatives have been synthesized and have been shown not to be identical with rubiadin and its derivatives.

	Rubiadin M. p., °C.	1,3-dihydroxy-4-methyl- anthraquinone M. p., °C.
Anthraquinone	290	251
Dimethyl ether	181	162
Diacetate	225	176.5

The only conclusion that can be drawn is that rubiadin is 1,3-dihydroxy-2-methylantraquinone and that Schunck and Marchlewski did not obtain the pure diacetate of 1,3-dihydroxy-2-methylantraquinone synthetically, and consequently found a discrepancy between the melting point of their product and that of the corresponding derivative of the natural product.

The 1,3-dihydroxy-4-methylantraquinone was prepared by condensing phthalic anhydride with 2,4-dichlorotoluene to give 2,4-dichloro-5-methylbenzoyl-*o*-benzoic acid (III), which was converted with sulfuric acid to the corresponding anthraquinone (IV). Upon long treatment with sodium methylate the halogens were replaced by methoxyl groups (V) and the free hydroxyl derivative was obtained by the action of hydrobromic acid.



The synthesis of 1,3-dihydroxy-2-methylantraquinone is now being studied.

Experimental Part

2,4-Dichlorotoluene.—To 90 cc. of cuprous chloride solution (prepared according to the method of Marvel and McElvain⁵) was added a solution of 20 g. of 2,4-diaminotoluene hydrochloride in 20 g. of concd. hydrobromic acid and 100 cc. of water. The solution was brought to a boil in a flask fitted with a mercury seal stirrer and a reflux

⁵ Marvel and McElvain, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. III, 1925, p. 33.

condenser and then without further heating, 180 cc. of 10% sodium nitrite solution was added, drop by drop. When all was added the mixture was steam distilled and the dichlorotoluene washed with sodium hydroxide solution, water, and then distilled in a vacuum; yield, 11.6 g. of product boiling at 195°. The chief difference between these directions and those which appear in the literature⁶ is that a much more dilute solution is employed and a tight container used to prevent volatilization.

2,4-Dichloro-5-methyl-benzoyl-*o*-benzoic Acid. III.—The general procedure used was that described by Fieser⁷ for preparing 4-methyl-benzoyl-*o*-benzoic acid. After condensing for eight hours 20 g. of phthalic anhydride, 69 g. of 2,4-dichlorotoluene and 50 g. of anhydrous aluminum chloride, there was obtained a thick, viscous substance which, however, readily crystallized from hot toluene and when pure, melted at 140°; yield, about 60%.

Anal. Subs., 0.1000: 2.15 cc. of 0.1530 *N* NaOH. Calcd. for $C_{18}H_{10}O_3Cl_2$: neut. equiv. 309. Found: 304.

2,4-Dichloro-1-methylanthraquinone. IV.—A mixture of 20 g. of 2,4-dichloro-5-methyl-benzoyl-*o*-benzoic acid with 4 g. of boric acid and 400 cc. of concd. sulfuric acid was heated on a water-bath for two hours. Upon pouring into water, there was obtained 7.5 g. of product which upon purification from chloroform formed bright yellow crystals and melted at 155°.

Anal. Subs., 0.2000; 13.7 cc. of 0.1 *N* AgNO₃. Calcd. for $C_{16}H_8O_2Cl_2$: Cl, 24.4. Found: 24.3.

2,4-Dimethoxy-1-methylanthraquinone. V.—A solution of sodium methylate was prepared by adding as much sodium to 250 cc. of absolute methyl alcohol as would dissolve in it at ordinary temperature. To this was added 6 g. of pure 2,4-dichloro-1-methylanthraquinone and the mixture heated under a reflux condenser on a water-bath for 24 hours. Water was then added, the methyl alcohol boiled off and the crude product filtered and dried. Upon purification from chloroform, it formed yellow needles melting at 162°.

Anal. Subs., 0.1500; CO₂, 0.3949; H₂O, 0.0611. Calcd. for $C_{17}H_{10}O_4$: C, 72.4; H, 4.98. Found: C, 72.0; H, 4.6.

2,4-Dihydroxy-1-methylanthraquinone.—The 2,4-dimethoxy-1-methylanthraquinone was refluxed for 12 hours in a mixture of constant-boiling hydrobromic and glacial acetic acids. The product was purified from benzene and then formed pale yellow needles, melting at 251°.

Anal. Subs., 0.1000; CO₂, 0.2612; H₂O, 0.0360. Calcd. for $C_{16}H_{10}O_4$: C, 70.84; H, 3.97. Found: C, 71.26; H, 4.03.

2,4-Diacetoxy-1-methylanthraquinone.—By refluxing 1 g. of 2,4-dihydroxy-1-methylanthraquinone with 20 cc. of acetic anhydride and 2 g. of freshly fused sodium acetate, there was obtained upon treatment with water the diacetyl derivative, which was purified by crystallization from acetic acid. It formed yellow needles melting at 176.5°.

Summary

The synthesis of 1,3-dihydroxy-4-methylanthraquinone has been completed and the substance has been shown not to be identical with rubiadin.

URBANA, ILLINOIS

⁶ Erdmann, *Ber.*, **24**, 2771 (1891).

⁷ Fieser, *Ref. 5*, Vol. IV, p. 75.

[CONTRIBUTION FROM THE MEAT INSPECTION LABORATORY, BUREAU OF ANIMAL INDUSTRY]

BOA CONSTRICTOR FAT

BY ROBERT H. KERR

RECEIVED MAY 9, 1927

PUBLISHED AUGUST 5, 1927

I. Source and Preparation of Material

The material used was obtained from the carcass of a large boa constrictor which had died from natural causes at the National Zoological Park, and consisted of egg-shaped masses of fat located along the intestines. These were chopped into fine bits, a small amount of sodium bicarbonate was added to the hashed mass and the whole heated over a free flame with constant stirring to a temperature of 125°. After being held at this temperature for a few minutes the rendered fat was filtered through a large folded filter. The rendered fat was a clear liquid of faint yellow color, and a peculiar and somewhat unpleasant odor. When cold it was a soft, yellowish solid.

II. Analysis of the Rendered Fat

M. p.	28.5°	Specific gravity at 100° (water	
Iodine no. (Hanus)	79.43%	at 15.5 = 1)	0.8629
Iodine no. of liquid fatty acids	113.17%	Saponification no.	196.83%
Refractive index at 40°	1.4619	Free fatty acids	0.17%

Identification of Unsaturated Acids

(a) **Highly Unsaturated Acid.**—The liquid fatty acids were dissolved in a mixture of equal parts of glacial acetic acid and ether, and bromine was added to the development of a permanent red color. A white precipitate appeared at once. This was filtered off and washed with cold ether. It proved to be insoluble in boiling ether, but was sparingly soluble in boiling benzene. It did not exhibit a definite melting point but turned brown and decomposed at 180–190°. As the amount of the material was not sufficient for further investigation, a larger amount was prepared by brominating the mixed fatty acids obtained from 10 g. of the fat. The precipitate was found to be insoluble in ether, alcohol and chloroform, and sparingly soluble in hot benzene. It decomposed at 180–190°. Analysis showed that it contained 70.15% of bromine. The bromine content corresponds to that of octobromostearic acid, indicating the presence of an acid corresponding to the formula $C_{18}H_{28}O_2$.

(b) **Linolic Acid.**—After the removal of the precipitate of octobromostearic acid, the acetic acid and excess of bromine were removed from the ether solution of the brominated acids by shaking in a separatory funnel with a solution of potassium iodide and sodium thiosulfate and then washing thoroughly with water. The ether was then evaporated and the residue dried in a vacuum. The dried residue was treated with successive small portions of ice-cold petroleum ether and the insoluble portion carefully washed with cold petroleum ether and finally dried. The residue was white and granular. It exhibited all of the characteristic properties of tetrabromostearic acid, including melting point and neutralization value, thus showing the presence of linolic acid.

(c) **Oleic Acid.**—The presence of oleic acid was demonstrated by examination of the residue remaining after the removal of the octo- and tetrabromostearic acids from

the brominated liquid acids. The physical characters, solubility and bromine content of this residue corresponded to those of dibromostearic acid.

Solid Acids

The separation of liquid and solid fatty acids by the lead salt-ether method gave 33.13% of solid acids, melting at 41.2° and having a mean molecular weight of 282.96, the latter being calculated from the neutralization value.

By fractional precipitation with magnesium acetate and crystallization from alcohol, two fractions melting at 64.0 and 58.0°, respectively, were obtained. Neutralization gave a calculated mean molecular weight of 281.7 for the fraction melting at 64.0° and of 264.6 for the portion melting at 58.0°. The quantity of material was not sufficient to permit the preparation of pure acids.

Summary

A specimen of boa-constrictor fat was prepared and examined. The unsaturated acids were found to consist of oleic acid, linolic acid and a highly unsaturated acid which formed an insoluble bromo addition product, tentatively identified as octobromostearic acid. The saturated acids evidently consisted of palmitic and stearic acids.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SECTION OF BIOCHEMISTRY OF THE MAYO FOUNDATION]

SOME HALOGEN AND HYDROXYL DERIVATIVES OF 2-OXO-DIHYDRO, 2-OXO-HEXAHYDRO-INDOLE-3-PROPIONIC ACID, AND OF 2-OXO-HEXAHYDROBENZOFURAN-3-PROPIONIC ACID

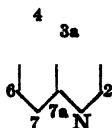
BY EDWARD C. KENDALL AND ARNOLD E. OSTERBERG

RECEIVED MAY 13, 1927

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The preparation of 2-oxo-hexahydro-benzofuran-3-propionic acid has been described.¹ If this compound is treated in dilute aqueous hydrobromic acid with bromine, a monobromo derivative can be separated (I). If a solution of the sodium salts of the lactone is treated with bromine a monobromo derivative of the lactone crystallizes from solution (II). These two monobromo derivatives are not identical; the one prepared from the sodium salt has the percentage composition of a monobromo derivative of the lactone. However, it is a neutral compound possessing no acidic properties although the carboxyl group in the original lactone requires one equivalent of sodium hydroxide for its neutralization.

¹ Kendall, Osterberg and MacKenzie, *THIS JOURNAL*, **48**, 1384 (1926). The indole nucleus is referred to by the following numbers, and the open pyrrolidine ring compounds are numbered in the usual manner for aromatic derivatives.



The monobromo derivative prepared in dilute hydrobromic acid contains a carboxyl group, and it is much more soluble than the one which shows no acidic properties. It can be crystallized from xylene, but if the solution is refluxed for about an hour water is given off and, after cooling, crystals separate which are identical with the neutral monobromo derivative (II). The percentage composition of the monobromolactone with acidic properties (I) corresponds to that of a monobromo derivative of the original lactone with the addition of one molecule of water.

Both of these bromolactones give the same hydroxyl derivative when treated with sodium hydroxide. This hydroxyl derivative also exists in two forms, acidic and neutral, which corresponds to the bromolactone. If the hydroxyl derivative is heated with a slight excess of sodium hydroxide, two equivalents of alkali are required for the neutralization of the product. The terminal carboxyl and the carboxyl group of the lactone both exist in free form (VI). If the disodium salt is treated with an equivalent amount of mineral acid and the solution is allowed to stand at room temperature, one equivalent of carboxyl titration disappears and then only one equivalent of sodium hydroxide is required for its neutralization; this is evidence for the closure of the lactone ring in a slightly acid solution (IV). If this solution is now boiled, the remaining acid group reacts in such a manner that the resulting solution is neutral (V).

Identification of these compounds could not be carried out until the position occupied by the bromine was determined. Oxidation with permanganate or with ozone did not give products which were useful for the identification of the compound. Further bromination did not result in the breaking of the lactone and did not give any products which were of help. Fusion with sodium hydroxide caused a deep-seated reaction and the products of the alkaline fusion indicate the position of the bromine. When the disodium salt of the hydroxyl compound is heated with concd. sodium hydroxide in a distilling flask to 170°, a volatile oil is given off. This is soluble in water, but can be thrown out of solution with potassium carbonate. It is only slightly soluble in ether and when recrystallized from benzene it proved to be the *trans*-form of cyclohexane glycol.² In the sodium hydroxide fusion were found large amounts of succinic acid. Only traces of acetic acid resulted from the fusion. If the heating was carried on at a higher temperature valeric acid was found in the fusion melt; no acid-insoluble product resulted.

These reactions indicate that the bromine occupied Position 3 and that the ketocyclohexane-hydroxyl-glutaric acid had rearranged, giving cyclohexane glycol (VII). The resulting α -hydroxyl-glutaric acid was broken down into carbon dioxide and succinic acid. No butyrolactone was formed, but the succinic acid was a high percentage of the amount

² Bedos, *Compt. rend.*, **183**, 750 (1926).

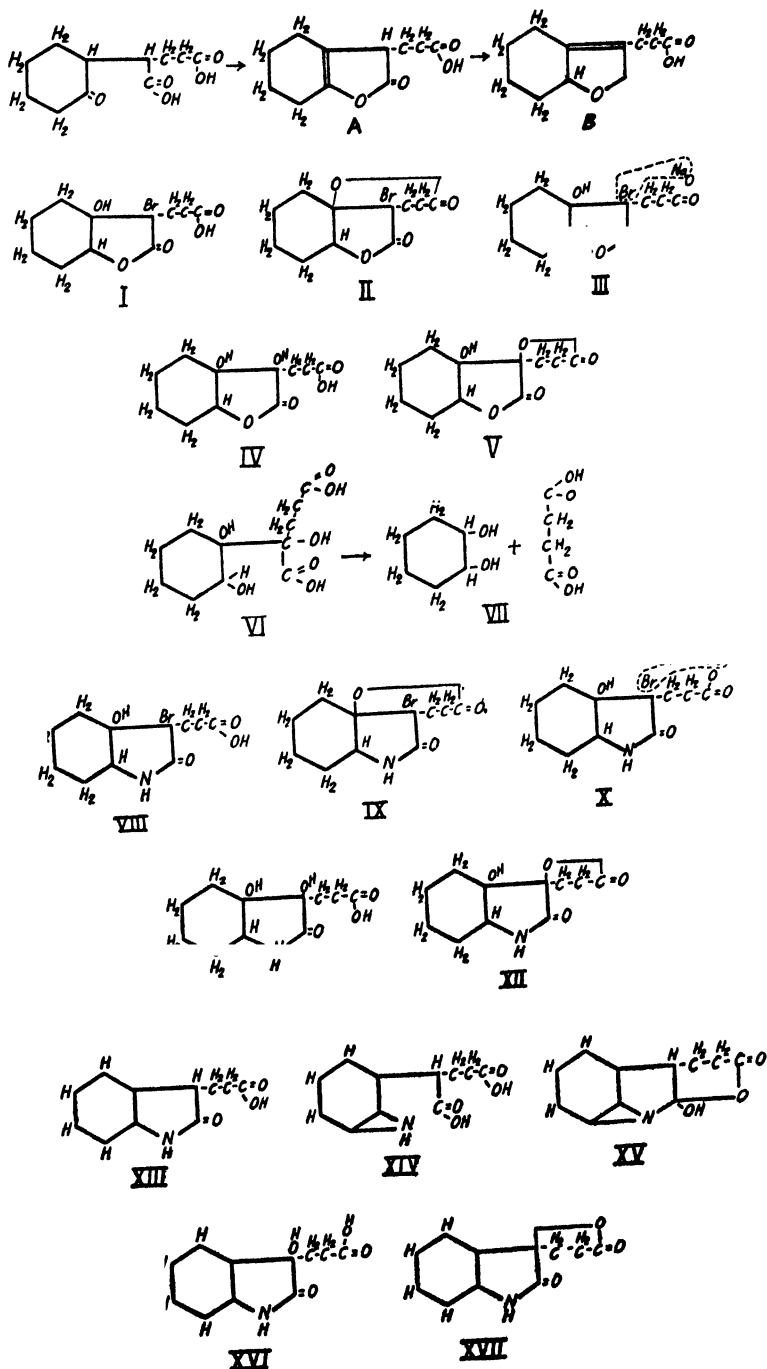
theoretically possible. Rupture of the cyclohexane ring probably explains the formation of the valeric acid at a high temperature.

After the identification of the position of the hydroxyl group in the lactone, it became necessary to explain the presence of the molecule of water in Form I and the loss of the carboxyl group in the neutral Form II. When two equivalents of bromine react with the sodium salt of the lactone one equivalent of bromine combines with the lactone, and the second equivalent is present in the solutions as sodium bromide. A yield of 90% of the monobromolactone was secured. This is conclusive evidence that the molecule of water is not present as an hydroxyl formed by oxidation of the lactone; still further evidence for this is the fact that the monobromolactone can easily be reduced to the original lactone, which separates without a molecule of water or an hydroxyl group.

When the monobromolactone is heated in xylene the resulting compound, which is neutral (II), is not formed by the loss of hydrobromic acid, but is formed by the loss of water. In connection with the problem of explaining these reactions, we take pleasure in acknowledging a suggestion from E. P. Kohler, who says, "First there is a shift of the double linkage from Δ -7a, 3a to Δ -3, 3a, as shown by Formulas A and B. This is the usual change of an unconjugated to a conjugated system of double bonds—probably the most general property of β,γ -unsaturated acids." Next, when the lactone B is treated with bromine in the presence of water, bromine does not substitute but hypobromous acid is added. "This is what invariably happens when an α,β -unsaturated acid or any of its derivatives or α,β -unsaturated ketones are treated with bromine in the presence of water or bases. In such cases bromine goes into the alpha position and hydroxyl into the beta."

The double bond in 2-oxo-hexahydrobenzofuran-3-propionic acid is very resistant to reduction or to the addition of hydriodic or hydrobromic acids and bromine. It reacts slowly with potassium permanganate. However, it seems most probable that the course of the bromination as suggested by Kohler is through the addition of hypobromous acid to the double bond which occupies Position 3,3a in the lactone. Closure to the lactone between the terminal carboxyl and the hydroxyl group on Position 3a explains the loss of acidic properties in the neutral Form II.

Another reaction which indicates that the disodium salt of the 3-hydroxyl derivative exists with hydroxyl groups on 3a and 7a, is the impossibility of forming the 3-hydroxyl-lactam from the 3-hydroxyl-lactone. Ketocyclohexane-glutaric acid will react with ammonia, giving a practically quantitative yield of the corresponding lactam, but when the 3-hydroxyl or the disodium salt of 3-hydroxyl-2-oxo-hexahydrobenzofuran-3-propionic acid is treated with ammonia no trace of lactam is produced. This is evidence that the ketone group is not present on Carbon 7a and that the structure probably is the 3,3a,7a-trihydroxyl derivative.



Conclusive proof of the structure of 2-oxo-hexahydrobenzofuran-propionic acid is furnished by the effect of ozone on this compound. Ozone reacts with this lactone in glacial acetic acid, with the formation of succinic acid. This decomposition could not occur unless the bond lay between Carbons 3 and 3a. Finally, if the 3-bromo-3a-hydroxyl derivative is treated with ozone no decomposition occurs. This is in agreement with the structure assigned, that is, a dihydroxyl derivative of octohydrobenzofuran.

The neutral form (II) of the monobromo derivative contains a δ -lactone, which is made by loss of water. If, however, the monobromolactone (I) is dissolved in a small amount of alcohol and water, and sodium hydroxide is added, it will remove most of the bromine attached to the lactone, and crystals separate from the solution (III). These crystals are neutral and are identical with the γ -lactone of the 3,3a-dihydroxyl derivative of the lactone (V). This is evidence that the second lactone grouping of this compound was made by loss of hydrobromic acid between the terminal carboxyl and the bromine attached to Carbon 3.

When the dihydroxyl derivative of the lactone (IV) is boiled in the presence of a small amount of mineral acid the γ -lactone derivative (V) separates from solution, and since this is identical with the compound made by loss of hydrobromic acid from the monobromolactone, the position of the second lactone ring in this compound probably is between the terminal carboxyl and the hydroxyl group attached to Carbon 3 (V). Still further evidence for this is the failure to substitute the hydroxyl group giving a lactone with halogen in Position 3 when the lactone derivative is treated with phosphorus oxychloride, phosphorus pentachloride and thionyl chloride.

These reactions indicate that the terminal carboxyl tends to form a lactone with the hydroxyl group in Position 3a if the hydrogen in Position 3 is substituted with bromine, but if an hydroxyl group is attached to Carbon 3 the terminal carboxyl forms a lactone with it.

The monobromolactone (I) reacts in a peculiar manner with sodium hydroxide. This is shown as follows. If to 100 mg. of the bromolactone 3.6 cc. of 0.1 *N* sodium hydroxide solution is added, the solution still reacts acid with phenolsulfonephthalein as indicator. If a total of 4 cc. is slowly added, all acidic properties are neutralized and the indicator becomes pink. At this hydroxyl-ion concentration, a second reaction is brought about and the alkalinity of the solution rapidly increases. Sulfuric acid, 0.1 *N*, can now be added until the solution reacts neutral, and this is soon followed by the liberation of more sodium hydroxide until a total of approximately 0.6 cc. of 0.1 *N* sulfuric acid has been added. Determination of the sodium bromide in the solution shows that only 1.9 cc. of 0.1 *N* sodium bromide is present; therefore, the increase in the alkalinity of the solution was due to closure of the lactone between the

terminal carboxyl and the hydroxyl group either on 3 or 3a. The total amount of alkali neutralized was 3.5 cc. of 0.1 *N*. The bromide removed was 1.9 cc., 0.1 *N*, which leaves 1.6 cc. of carboxyl neutralized with sodium hydroxide.

The relation between the sodium hydroxide required and the hydrobromic acid neutralized is evidence of lactone formation brought about by the sodium hydroxide. This was confirmed by separation of crystals of the γ -lactone of the 3,3a-dihydroxyl derivative (V). If, however, the sodium hydroxide first removes the bromine from Carbon 3, replacing it with hydroxyl, there is no evidence that the terminal carboxyl forms a lactone with an hydroxyl group on either Carbon 3 or 3a, at room temperature.

2-Oxo-hexahydro-indole-3-propionic acid¹ reacts with bromine in a manner entirely similar to the corresponding lactone. If the bromine is added to an aqueous solution of the lactam, the monobromolactam separates (VIII) and if the lactam is present as a monosodium salt in a solution containing sodium acetate the δ -lactone of the monobromo derivative separates (IX). It is, however, much easier to open the δ -lactone of the bromolactam than of the bromolactone. The last-mentioned compound can be heated in concd. hydrobromic acid without opening the second lactone ring. With the bromolactam the presence of even a small amount of mineral acid will bring about this reaction at room temperature. For each equivalent of bromine added to the lactam one equivalent of sodium bromide is formed. The bromine can be reduced from the monobromolactam with formation of the original material. Treatment with sodium hydroxide replaces the bromine forming the dihydroxyl derivative which exists in two forms (XI and XII) corresponding to the bromolactam.

Fusion of the 3,3a-dihydroxyl-lactam with sodium hydroxide decomposes this compound giving products similar to those obtained from the corresponding hydroxyl-lactone with sodium hydroxide. Succinic and acetic acids were identified, and an amine which precipitates from ether solution with carbon dioxide. Its chemical properties closely simulate those of *o*-aminocyclohexanol,² but insufficient material was obtained for its identification. The formation of this compound would correspond to the production of cyclohexane glycol from the hydroxyl-lactone. In addition to these compounds a volatile, crystalline substance was obtained which appeared to be a dimolecular derivative of the hydro-indole, $C_{11}H_9N$. No valeric or other acid-insoluble products were formed. These reactions are evidence that the hydroxyl groups are attached to Carbons 3 and 3a, and that the dihydroxyl-lactam decomposes in two ways, one giving succinic acid and a derivative of cyclohexane, the other giving a hydro-indole

¹ Osterberg and Kendall, *THIS JOURNAL*, **42**, 2616 (1920). Brunel, *Ann. chim. phys.*, **6**, 253 (1905).

derivative and malonic acid which decomposes into carbon dioxide and acetic acid.

In the lactone of the dihydroxyl derivative of the lactam (XII) the terminal carboxyl is probably combined with the hydroxyl group on Carbon 3. Evidence for this is the impossibility of forming the 3-halogen derivative of the lactam by treatment of the lactone of the dihydroxyl-lactam with phosphorus pentachloride, phosphorus oxychloride or thionyl chloride. Further evidence for this is the preparation of the γ -lactone by boiling the dihydroxyl-lactam (XI) in mineral acid. It is impossible to close the δ -lactone of the bromolactam by heating in acid. The γ -lactone of the 3,3a-dihydroxyl derivative is also made from the 3-bromo-3a-hydroxyl-lactam (VIII) with sodium hydroxide (X).

Reactions of 2-Oxo-dihydro-3-propionic Acid with Halogen.—Mono-, di- and trihalogen derivatives of 2-oxo-dihydro-indole-3-propionic acid have been described.¹ At that time a tentative formula was given for these compounds.

Further work with this series of compounds has indicated the structures of the two forms of the halogen and hydroxyl derivatives of the hexahydrolactones and lactams, and investigation of the decomposition products of the derivatives of 2-oxo-dihydro-indole-3-propionic acid has resulted in identification of the positions held by the entering halogens and the chemical properties are satisfactorily explained by the following structures. The position first substituted in 2-oxo-dihydro-indole-3-propionic acid is the hydrogen attached to Carbon 3. If two equivalents of iodine are added to the sodium salt of the lactam, all the iodine is found in solution as sodium iodide and crystals may be separated which contain no iodine. This crystalline compound exists in two forms apparently similar to the lactones and lactams described. When treated with hydriodic acid it shows oxidizing power. Since the chemical properties and percentage composition of this substance correspond to the original lactam with the addition of a molecule of water and loss of two atoms of hydrogen, the original structure assigned was an open pyrrolidone ring with a bond between Carbon 7 and the nitrogen (XIV). The neutral form was assigned a lactone structure somewhat similar to the neutral forms of the lactams already described (XV).

Definite evidence for the structure of this compound is furnished by fusion with sodium hydroxide. The original lactam (XIII) heated in an atmosphere of hydrogen with sodium hydroxide to a temperature of 200° can be recovered unchanged. The product obtained after treating the lactam with two equivalents of iodine decomposes under similar conditions and aniline⁴ is volatilized from the fusion flask. This is evidence that Carbon 3 is the point of attack, and the 3-hydroxyl derivative of the original

⁴ Hofmann, *Ann.*, 53, 11 (1845).

lactam is the probable structure of the product obtained after treatment with iodine (XVI). When this compound is heated it loses water and a γ -lactone is formed between the terminal carboxyl and the 3-hydroxyl group with loss of acidic properties (XVII). Such a compound would not add bromine or ozone to a double bond, but could react with hydrobromic acid and could be reduced with hydriodic acid or sodium amalgam.

When the 3-hydroxyl-lactam is treated with methyl sulfate a dimethyl derivative is obtained. One methyl group is attached to the hydroxyl and the second methyl group is presumably attached to the nitrogen, but only one methyl group can be determined with hydriodic acid, as the second methyl group apparently migrates from the nitrogen and is then stable to hydriodic acid.

If the dibromo or di-iodo derivative of this lactam is brominated,¹ the bromine enters a position in which it is exceedingly unstable. This trihalogen compound will lose hydrobromic acid in acetic acid with sodium acetate or in alcoholic solution with cold dil. sodium hydroxide. The resulting product is neutral, and has a percentage composition of a γ -lactone of a dihalogen derivative of the 3-hydroxyl-lactam. The bromine apparently substitutes the hydrogen in Position 3. This is confirmed by the result of alkaline fusion; a volatile oil was obtained which after purification proved to be 2,4-dibromo and 2,4-di-iodo-aniline.⁵

When 2-oxo-dihydro-indole-3-propionic acid is treated with bromine, Position 3 appears to be the primary point of attack; however, it is possible to prepare the 3-hydroxyl-lactam, and the γ -lactone of this compound will form a monobromo substitution product. The only point of interest of this compound is the position occupied by the bromine. Since the compound is easily decomposed with alkali it is difficult to separate sufficient of the monobromo-aniline for purposes of identification; this fact, however, suggests that the bromine occupies position 5 in the indole derivative, and is, therefore, *para* to the amine group. Bromine in the *para* position to the nitrogen is much less stable to alkaline fusion than it is in the *ortho* position. The traces which were separated melted too high for the *o*-bromo-aniline, although it was impossible to purify it sufficiently to obtain a sharp melting point which agreed with the *p*-monobromo-aniline.

The structures of the three halogenated compounds are, therefore, 5-monobromo-, 5,7-dibromo- and 3,5,7-tribromo-2-oxo-dihydro-indole-3-propionic acid.

A remarkable property of this series of compounds is the ease with which the hydrogen of Carbon 3 is oxidized to hydroxyl. In a slightly alkaline solution molecular oxygen will oxidize this lactam and at a *PH* of 7.4, dibromo-indophenol will bring about this oxidation. The details of this

⁵ Ref. 4, p. 47.

reaction have been described elsewhere,⁶ and further investigations of this reaction will be reported in the near future.

Experimental Part

Five determinations have been applied to the compounds described in the Experimental Part. (1) The "direct titration" is the amount of 0.1 *N* sodium hydroxide solution required to neutralize carboxyl groups. This has been determined in alcohol with a 100mg. sample and with phenol-sulfonephthalein as indicator. (2) The "total titration" is the amount of 0.1 *N* sodium hydroxide solution neutralized by 100 mg. of the material after it has been boiled for five minutes with 15 cc. of 0.1 *N* sodium hydroxide solution, and the solution has been back-titrated with 0.1 *N* sulfuric acid. Phenolsulfonephthalein has also been used as indicator in this titration. (3) The "halogen removed" is the halogen in the solution removed by alkali. It has been determined with 0.1 *N* silver nitrate by the method of Volhard. This titration has been made after the solution has been boiled with alkali and acidified with nitric acid. (4) The "cold oxidizing power" is the amount of 0.1 *N* iodine liberated by adding 100 mg. of the compound to a cold solution of 2 g. of potassium iodide and 2 cc. of 1:1 hydrochloric acid contained in 15 cc. of glacial acetic acid. The iodine set free was titrated with 0.1 *N* sodium thiosulfate solution. (5) The "total oxidizing power" is the total amount of iodine liberated by 100 mg. of material. It has been determined by adding the substance to the acetic acid solution of potassium iodide and hydrochloric acid, and then boiling the solution under an inside reflux condenser for five minutes. After the solution has been boiled, it is removed as rapidly as possible from under the reflux and immediately cooled. Water is added until the volume is approximately 100 cc. and the free iodine is determined by 0.1 *N* sodium thiosulfate, with starch as indicator. Unless the solution is cooled rapidly after the refluxing, atmospheric oxygen will liberate iodine. These five determinations will be described as "direct titration" for carboxyl; "total titration" for total acid groups; "halogen removed" for inorganic halogen after boiling with 15 cc. of 0.1 *N* sodium hydroxide; "cold oxidizing power," and "total oxidizing power" for the iodine liberated from hydriodic acid. All melting points are uncorrected.

2-Oxo-3-bromo-3 α -hydroxyl-octahydrobenzofuran-3-propionic Acid (I).—One-twentieth mole (10.5 g.) of 2-oxo-2,3,4,5,6,7-hexahydrobenzofuran-3-propionic acid is dissolved in 200 cc. of hot water and poured into a 500cc. glass-stoppered bottle containing 6 cc. of 9 *N* hydrobromic acid; 2.5 cc. of bromine is added, the bottle tightly stoppered, shaken, placed in a beaker of water on a steam-bath, and heated until no free bromine is present. The solution is concentrated in a vacuum to about 30 cc. The crystals which separate are filtered, thoroughly washed, and dissolved in 50 cc. of alcohol to which 150 cc. of water is added. The solution is allowed to stand for about one hour,

⁶ Kendall, and Ort, *J. Biol. Chem.*, **68**, 611 (1926).

A small amount of the δ -lactone form of the bromolactone may separate. This is filtered off and the solution concentrated in a vacuum. Crystals again separate from the solution, are filtered, washed and dried; yield, about 50%; m. p., 147°.

Anal. Calcd. for $C_{11}H_{13}O_4Br$: C, 42.99; H, 4.92; Br, 26.03. Found: C, 42.71; H, 4.85; Br, 26.00.

Direct titration, 4.8; total titration, 9.9; halogen removed, 3.3 cc.; oxidizing power, 6.4 cc.

To prepare the δ -lactone form, 2.9 g. of the monobromolactone is dissolved in 100 cc. of boiling xylene, which is refluxed for one hour; after standing for several hours crystals separate; yield, 1.9 g. These are treated with 5 cc. of alcohol to dissolve any unchanged material. Thirty cc. of water is then added and the solution filtered. The crystals recrystallized from xylene are identical with the δ -lactone form (II), m. p. 144°, and when mixed with the δ -lactone of the monobromolactone the melting point is unchanged.

δ -Lactone of 2-Oxo-3-bromo-3a-hydroxyl-octohydrobenzofuran-3-propionic Acid (II).—One-tenth mole (20.9 g.) of 2-oxo-2,3,4,5,6,7-hexahydrobenzofuran-3-propionic acid is dissolved in 300 cc. of water containing 20 cc. of 5 *N* sodium hydroxide and 5.3 g. of sodium carbonate. To this is slowly added 5.5 cc. of bromine. The solution is allowed to stand for 18 hours. The crystals which separate are filtered, washed and air dried; yield, 90%; m. p., 144°.

Anal. Calcd. for $C_{11}H_{13}O_4Br$: C, 45.67; H, 4.53; Br, 27.65. Found: C, 45.40; H, 4.46; Br, 27.25.

Direct titration, none; total titration, 10.6 cc.; halogen removed, 3.4 cc.; cold oxidizing power, none; total oxidizing power, 7.0.

2-Oxo-3,3a-dihydroxyl-octohydrobenzofuran-3-propionic Acid (IV).—The γ -lactone of the 3,3a-dihydroxyl-lactone (V) is dissolved in an excess of warm sodium hydroxide solution. The sodium hydroxide is then neutralized with just an equivalent amount of sulfuric acid and the solution is concentrated in a vacuum. After standing for a short time crystals separate; m. p., 164°; direct titration, 4.1 cc.; total titration, 8.6 cc.; oxidizing power, none. If this substance is boiled with 15 cc. of 0.1 *N* sulfuric acid, the solution will back-titrate 15 cc. of 0.1 *N* sodium hydroxide, and the γ -lactone of this derivative can be separated from solution.

γ Lactone of 2-Oxo-3,3a-dihydroxyl-octohydrobenzofuran-3-propionic Acid (V).—One-tenth mole (29 g.) of 3-bromo-3a-hydroxyl-octohydrobenzofuran-3-propionic acid is dissolved in 200 cc. of 1 *N* sodium hydroxide solution and heated to boiling. The solution is made slightly acid with 11 cc. of 10 *N* sulfuric acid and is boiled for 20 minutes. On cooling, crystals of the γ -lactone of the 3,3a-dihydroxyl derivative of the lactone separate. These may be recrystallized from aqueous alcohol; m. p., 146°.

Mol. wt. Subs., 0.2017; in C_6H_5OH , 15.07; Δt , 0.412°. Calcd. for $C_{11}H_{14}O_4$: mol. wt., 226. Found: 246.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 58.38; H, 6.24. Found: C, 58.34; H, 6.12.

Direct titration, none; total titration, 9.0 cc.; oxidizing power, none.

The γ -lactone of the 3,3a-dihydroxyl-lactone is prepared as follows.

One g. of the 3-bromo, 3a-hydroxyl-lactone is dissolved in a small amount of alcohol, to which 100 cc. of water is added. To this, 4 cc. of 1 *N* sodium hydroxide solution is added and the solution is concentrated in a vacuum. It is allowed to stand for several hours; crystals which separate are removed by filtration. After washing and drying, these crystals are identical with the γ -lactone of the 3,3a-dihydroxyl derivative of the lactone.

2-Oxo-3-bromo-3a-hydroxyl-octohydro-indole-3-propionic Acid (VIII).—One-

twentieth mole (10.5 g.) of the lactam is dissolved in 200 cc. of boiling water. The hot solution is poured into a pressure bottle containing 6 cc. of constant-boiling hydrobromic acid; 2.5 cc. of bromine is added by allowing the bromine to run down the side of the bottle. The stopper is quickly clamped and the contents are well shaken. Most of the bromine disappears in a few minutes and crystals separate as the solution cools. These are filtered, washed and dried; yield, 12 g.; m. p., 156°.

Anal. Calcd. for $C_{11}H_{14}O_4NBr$: C, 43.13; H, 5.27; Br, 26.11. Found: C, 43.12; H, 5.25; Br, 25.90.

Direct titration, 3.4 cc.; total titration, 6.8 cc.; halogen removed, 3.3 cc.; total oxidizing power, 6.5 cc.

It is impossible to make the δ -lactone of the 3-bromolactam by heating this substance in xylene. The solution becomes brown, and the bromolactam rapidly decomposes.

δ -Lactone of 2-Oxo-3-bromo-3a-hydroxyl-octahydro-indole-3-propionic Acid (IX).—One-tenth mole (21 g.) of 2-oxo-2,3,4,5,6,7-hexahydro-indole-3-propionic acid is dissolved in 100 cc. of water by the addition of 20 cc. of 5 *N* sodium hydroxide solution. To this is added 5 cc. of bromine in 100 cc. of 2 *N* sodium hydroxide solution. With agitation, 40 cc. of 5 *N* sulfuric acid is then added. The free bromine which has not reacted is removed in a vacuum and the crystals are filtered off; yield, 17 g.

An alternative method is to dissolve 0.1 mole of the lactam in water containing one equivalent of sodium hydroxide. The solution is made to contain 25% of acetic acid with a volume of about 300 cc. by the addition of acetic acid. By means of an air stream, 5 cc. of bromine is then aerated into the cold solution. Crystals separate in a few minutes; yield, 20 g. These crystals are the δ -lactone of the 3-bromo-3a-hydroxyl-lactam; m. p., 153°.

Anal. Calcd. for $C_{11}H_{14}O_5NBr$: C, 45.83; H, 4.90; Br, 27.76. Found: C, 45.77; H, 4.84; Br, 28.00.

Direct titration, none; total titration, 7.2 cc.; halogen removed, 3.5 cc.; cold oxidizing power, none; total oxidizing power, 7.0 cc.

2-Oxo-3,3a-dihydroxyl-octahydro-indole-3-propionic Acid (XI).—Fourteen g. (0.05 mole) of the 3-monobromo-3a-hydroxyl-lactam (VIII or IX) is dissolved in 40 cc. of 5 *N* sodium hydroxide solution, and the solution is warmed to 60°. After cooling, 42 cc. of 5 *N* sulfuric acid is added and the crystals which separate are filtered off; yield, 7.3 g.; m. p., 180°.

Anal. Calcd. for $C_{11}H_{17}O_6N$: C, 54.29; H, 7.04. Found: C, 54.37; H, 6.89.

Mol. wt. Subs., 0.1500; in C_6H_5OH , 12.66; Δt , 0.42°. Calcd. for $C_{11}H_{18}O_4N$: mol. wt., 225. Found: 213.

γ -Lactone of 2-Oxo-3,3a-dihydroxyl-octahydro-indole-3-propionic Acid (XII).—When the 3,3a-dihydroxyl-lactam is dissolved in boiling dilute mineral acid, the γ -lactone (XII) crystallizes from solution. The compound may be recrystallized from aqueous alcohol; m. p., 206°.

Anal. Calcd. for $C_{11}H_{16}O_5N$: C, 58.64; H, 6.66. Found: C, 57.96; H, 6.58.

Direct titration, none; total titration, 5.2 cc.; total oxidizing power, none.

This compound can be made from the 3-monobromo-3a-hydroxyl-lactam with dil. sodium hydroxide solution. One g. of the 3-monobromolactam is dissolved in a small amount of alcohol and water. To this, 4 cc. of 1 *N* sodium hydroxide is added. The solution is concentrated and allowed to stand. The crystals are filtered, washed and recrystallized from alcohol and water; m. p., 206°. When mixed with the γ -lactone of the 3,3a-dihydroxyl-lactam, the melting point is unchanged.

Formation of Cyclohexadiene Glutaric Acid from 2-Oxo-hexahydrobenzofuran-

3-propionic Acid with Sodium Hydroxide.—Ten g. of 2-oxo-hexahydrobenzofuran-3-propionic acid is heated with 50 cc. of saturated sodium hydroxide solution in a 300cc. Pyrex distilling flask, through which oxygen-free hydrogen is continually passed. The flask is immersed in a Woods' metal bath maintained at 180 to 200°. Water is driven out of the flask, and the contents crystallize to a solid, white mass. This is dissolved in water and when made acid with sulfuric acid crystals separate. These are purified from boiling water; yield, 75%; m. p., 219°; direct titration, 9.3 cc.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.82; H, 6.71. Found: C, 62.30; H, 6.44.

This compound slowly adds two atoms of bromine in acetic acid solution. The bromo addition product easily decomposes with loss of hydrobromic acid.

Formation of trans-Cyclohexane Glycol, Succinic Acid and Valeric Acid from 3,3a-Dihydroxyl-2-oxo-octohydrobenzofuran-3-propionic Acid.—Ten g. of the 3,3a-dihydroxyl derivative of the lactone is dissolved in 15 cc. of water containing a small amount of sodium hydroxide. To this is added 50 cc. of saturated sodium hydroxide solution. The flask is heated in a Woods' metal bath to 200° and oxygen-free hydrogen is passed through the flask. The water which volatilizes from the solution is saturated with potassium carbonate. A small amount of oil separates from the water which is removed and extracted with hot benzene. After evaporating the benzene to small volume, crystals separate; purified by recrystallization from benzene, m. p. 104°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 62.01; H, 10.41. Found: C, 62.03; H, 9.82.

The melting point of the dibenzoyl derivative is 93°. The dibenzoyl derivative of *trans*-cyclohexane glycol prepared from cyclohexane oxide with water melted at 93°. When mixed with the dibenzoyl derivative of the glycol prepared from the alkaline fusion of the hydroxyl-lactone, the melting point was unchanged.

SEPARATION OF SUCCINIC ACID.—The fusion melt in the flask, after the temperature reaches 200°, is dissolved in water and made acid with hydrochloric acid. The solution is evaporated to dryness and the sodium chloride residue and organic material are extracted with ether. The ether is evaporated to dryness and the residue purified by crystallization from water; m. p., 185°.

Neut. equiv. Subs., 0.1000: 16.90 cc. of 0.1 *N* alkali. Calcd. for $C_4H_4O_4$: 16.94 cc.

The *p*-toluide melts at 255°. The boiling point and saponification number of the diethyl ester of this acid agree with those of diethyl succinate.

VALERIC ACID.—When the alkaline fusion of the 3-hydroxyl derivative of the lactone is heated to 300° in an atmosphere of hydrogen a volatile acid passes over with steam after the fusion melt has been acidified with hydrochloric acid. The acid is not easily soluble in water; it separates in oily drops. The aqueous distillate is extracted with ether and the ether is removed by distillation. The residue in the flask is distilled; 0.1100 g. required 10.2 cc. of 0.1 *N* sodium hydroxide, indicating a molecular weight of approximately 100. The acid chloride prepared by means of thionyl chloride may be converted to the acid amide with aqueous ammonia. The acid amide separates from the ammoniacal solution with potassium carbonate and on recrystallization from ether melts at 114°.

Anal. Calcd. for $C_5H_{11}ON$: N, 13.8. Found: 13.6.

Formation of an Indole Derivative, Succinic and Acetic Acids, from 2-Oxo-3,3a-dihydroxyl-octohydro-indole-3-propionic Acid with Sodium Hydroxide.—Sodium hydroxide converts 2-oxo-hexahydro-indole-3-propionic acid quantitatively into 2-keto-cyclohexane-1- α -glutaric acid, which is then changed into cyclohexadiene glutaric acid with alkaline fusion. The 3,3a-dihydroxyl derivative of 2-oxo-hexahydro-indole-3-propionic acid loses only a small amount of its nitrogen as ammonia when fused with sodium hydroxide. Ten g. of the 3,3a-dihydroxyl derivative is heated in the presence

of hydrogen in a 300cc. Pyrex flask, with 50 cc. of saturated sodium hydroxide, after the lactam has been dissolved in 15 cc. of water with a small amount of sodium hydroxide. When the temperature reaches about 170° a volatile oil, which crystallizes, distills with the water. The crystals are separated by extraction with ether and may be crystallized from a mixture of alcohol and water; m. p., 132°.

Anal. Calcd. for $C_8H_{11}N$: C, 79.28; H, 9.16; N, 11.57. Found: C, 79.39; H, 8.80; N, 10.64.

Mol. wt. Subs., 0.1392; in C_6H_5OH , 12.42: Δt , 0.468°. Calcd. for $C_{16}H_{22}N_2$: mol. wt., 242. Found: 182.

This compound in acid solution forms a bromine addition product which is decomposed in boiling water with the liberation of the original material, and bromine does not substitute hydrogen. The positions of the bonds in the molecule were not identified.

Sodium hydroxide separates an amine from the water which distills from the fusion flask. The oil is extracted with ether and if carbon dioxide is passed through the dried ether solution a precipitate is formed. This may be redissolved in water, precipitated with sodium hydroxide and re-extracted with ether. Its chemical properties suggest that it is *o*-aminocyclohexanol.

SUCCINIC ACID.—Succinic acid was separated from the sodium hydroxide fusion in a manner entirely similar to the isolation of this material from the 3-hydroxyl-lactone. It was identified by melting point, carboxyl titration and the toluides.

ACETIC ACID.—From the aqueous solution of the sodium hydroxide fusion a volatile acid is obtained after acidification with hydrochloric acid. Sodium hydroxide is added to the distillate and the solution evaporated to dryness. Sirupy phosphoric acid and ether are added to the beaker and the organic acid extracted with the ether. The ether is removed and the *p*-toluide prepared. Its melting point, 147°, is that of acetic acid toluides.

Fusion of 2-Oxo-dihydro-indole-3-propionic Acid with Sodium Hydroxide.—Ten g. of this lactam is heated in a 300cc. Pyrex distilling flask in an atmosphere of hydrogen with 50 cc. of saturated sodium hydroxide solution, after the material has been dissolved in a few cubic centimeters of water containing sodium carbonate. The atmosphere of hydrogen prevents oxidation of the lactam. The heating is carried out at 200° for one hour. The solution is cooled and water added in the presence of hydrogen. The solution of the fusion mass is made acid with hydrochloric acid. The original lactam precipitates unchanged.

Formation of Aniline from 3-Hydroxyl-2-oxo-dihydro-indole-3-propionic Acid.—When the 3-hydroxyl derivative is fused under similar conditions, a volatile oil is given off at about 210°. The oil is extracted with ether and treated with acetic anhydride. The acetyl derivative is purified by crystallization from hot water; m. p., 114°. The 5,7-dibromo derivative of the 3-hydroxyl-lactam decomposes with sodium hydroxide at 170–180°. The volatile oil is purified by steam distillation, and crystallized from alcohol and water; m. p., 79°; acetyl derivative, m. p. 146°. This agrees with the melting point of 2,4-dibromo-aniline and its acetyl derivative.

Anal. Calcd. for $C_8H_8NBr_2$: Br, 63.70. Found: 63.71.

The 5,7-di-iodo-3-hydroxyl derivative of this lactam, fused with sodium hydroxide, gives an oil which is crystallized from alcohol and water; m. p., 95°. When mixed with 2,4-di-iodo-aniline the melting point was unchanged.

Anal. Calcd. for $C_8H_8NI_2$: I, 73.59. Found: 73.15.

Methylation of 3-Hydroxyl-5,7-dibromo-2-oxo-dihydro-indole-3-propionic Acid.—Seven and two-tenths g. of the γ -lactone of 5,7-dibromo-3-hydroxyl-2-oxo-dihydro-

indole-3-propionic acid is dissolved in 40 cc. of 2 *N* potassium hydroxide solution, and treated with 24 cc. of dimethyl sulfate and 40 cc. of 6.5 *N* sodium hydroxide solution. The dimethyl sulfate and alkali are added alternately in 2cc. portions with vigorous shaking after each addition. Twenty cc. of 10 *N* sodium hydroxide is added and the products are saponified by boiling for 90 minutes. The solution is made acid and the semi-solid precipitate washed a few times in water. This is dissolved in 95% alcohol and diluted to approximately 50% with water. Crystals separate; yield, about 75%; m. p., 140°.

Anal. Calcd. for: $C_{13}H_{13}O_4NBr_2$: C, 38.32; H, 3.21; Br, 39.26. Found: C, 38.31; H, 3.21; Br, 39.00.

Direct titration, 2.5 cc.; total titration, 2.5 cc.; halogen removed, none; oxidizing power, none.

The methyl groups were determined according to the Zeisel micro method.

Anal. Calcd. for $2CH_3$, 7.37; $1CH_3$, 3.65. Found: CH_3 , 3.65.

The ultimate analyses for carbon, hydrogen and bromine indicate the presence of two methyl groups, but as only one can be removed with hydriodic acid it seems probable that the hydroxyl group on Carbon 3 is reduced by the hydriodic acid, and that the methyl attached to the nitrogen then migrates probably to Position 3 and is stable to hydriodic acid under conditions which will remove a methyl group attached to nitrogen.

Summary

2-Oxo-hexahydro-indole-3-propionic acid and its corresponding lactone react with hypobromous acid forming monobromo, monohydroxyl derivatives in which the bromine substitutes the hydrogen in Position 3 and the hydroxyl group is attached to Position 3a. The terminal carboxyl will form a δ -lactone with the hydroxyl group on Carbon 3a.

The bromine in these halogen derivatives can be replaced with hydroxyl by treatment with sodium hydroxide. These dihydroxyl derivatives form γ -lactones between the terminal carboxyl and the hydroxyl group on Carbon 3. They do not form δ -lactones.

2-Oxo-dihydro-indole-3-propionic acid and its mono- and dihalogen derivatives are easily oxidized, resulting in the formation of an hydroxyl group on Carbon 3. The hydroxyl group of these compounds will form a γ -lactone with the terminal carboxyl group.

The positions occupied by the bromine in the mono-, di- and tribromo derivatives of 2-oxo-dihydro-indole-3-propionic acid which have been described in a previous publication¹ have been determined. These halogen derivatives are 5-mono-, 5,7,di- and 3,5,7,-tribromo-2-oxo-dihydro-indole-3-propionic acid, respectively.

ROCHESTER, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

KENTUCKY COFFEE NUT TREE SEED OIL¹

BY CHARLES BARKENBUS AND ALEC J. ZIMMERMAN

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The Kentucky coffee nut tree (*Gymnocladus dioica*) grows over an area extending from central New York westward to Minnesota and southward to the Tennessee line. It is not a common tree and probably grows most abundantly in the State after which it is named. The pods from this tree measure from 8 to 15 cm. in length and have from three to six seeds imbedded in a mucilaginous material. The black seed coating is exceptionally hard and the seed itself is very compact. The average weight of the seeds is about 2.5 g.

The sweet mucilaginous material in the pods is considered by some people to be poisonous, but only brief reports of the poisonous nature could be found in the literature. Cytisine is reported by Chesnut² in the leaves and the mucilaginous material of the pods. A saponin and a toxalbumin are reported to be present in the seeds.³ The same authors report deaths from eating the unroasted seeds but no references are given.

Only very meager reports can be found on the chemical examination of the pods and the seed. Stone and Test⁴ examined the mucilaginous material of the pods for carbohydrates and found glucose and sucrose in large quantities. The insoluble part of the material was provisionally called a gluco-araban. Approximate analysis of the seed and some of the constants of the oil from the seeds has been made.³

Since very little work has been done on the chemical examination of the seeds and the pod, we are subjecting them to a complete examination. This paper deals with the analysis of the oil from the seeds and includes an approximate analysis of the seeds and the pods.

The pods were collected in Fayette County, Kentucky, in the fall of 1923. The seeds were separated from the pods and the pods were air-dried and ground. The seeds were shelled, ground and extracted at once. Most of the work was done one year after collecting but due to an unavoidable delay the results have not been ready for publication.

Experimental Part

Quantitative extractions were made as shown in Table I.

The analysis was made by the official methods. The sugar by inversion is rather high for both the seed and the pod.

¹ Read before The Kentucky Academy of Science, May 7, 1927.

² Pammel, "Manual of Poisonous Plants," The Torch Press, Cedar Rapids, Ia., 1911, p. 537.

³ Watson and Sayre, *J. Am. Pharm. Assoc.*, 6, 601 (1917).

⁴ Stone and Test, *Am. Chem. J.*, 15, 660 (1893).

TABLE I
QUANTITATIVE EXTRACTIONS

	Seed, %	Pod, %
Petroleum ether (50–60°)	19 27	0 41
Ether	19 92	1 24
Alcohol (95%)	49 00	42 05

TABLE II
APPROXIMATE ANALYSIS

	Seed, %	Pod, %		Seed, %	Pod, %
Moisture	5.98	11.41	Free invert sugar	0.00	3.56
Ash	3.85	3.18	Sugar by inversion	12.06	18.95
Protein (N, 6.25)	32.30	6.50	Pentosans	5.67	17.29
Crude fiber	2.01	21.12	Starch (diastase)	13.32	18.91

Physical and Chemical Examination of the Oil from the Seeds

The oil was obtained by extracting 2360 g. of the shelled, ground seed with absolute ether. The last traces of ether were removed by heating in a vacuum. Four hundred and eighty g. of a clear, light yellow oil with a bland taste was obtained. On standing, the oil deposited a small amount of solid. The oil is practically odorless. The physical and chemical properties are given in Table III.

TABLE III
PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE OIL

d_{20}^{20}	0 9219
n_D^{20}	1.4769
Iodine no. (Hanus)	137.5
Saponification value	191.03
Reichert-Meissl no.	0.44
Acid value	0.39
Acetyl value	11.35
Unsaponifiable matter, %	1.28
Soluble acids (% of butyric acid)	0.83
Insoluble acids, %	93.93 (Iodine no., 132.0)
Unsaturated acids (corr.), %	89.74 (Iodine no., 145.0)
Saturated acids (corr.), %	4.86 (Iodine no., 3.4, before correcting)

The iodine number would indicate a semi-drying oil but only a trace of a film was developed on exposure to the air on a glass plate for a week.

The low Reichert-Meissl number shows that only a trace of glycerides of the lower fatty acids is present, while the low acetyl value indicates a small amount of glycerides of the hydroxylated acids. The oil does not become rancid readily. The saturated and unsaturated acids were obtained by the lead salt-ether method, using the usual precautions and corrections.⁵ The percentage of saturated acids is rather low.

⁵ Baughman, Brauns and Jamieson, *THIS JOURNAL*, **42**, 2398 (1920).

Unsaturated Acids

The bromine addition compounds of the unsaturated acids were made.⁶ No hexabromide was obtained, showing the absence of linolenic acid. The precipitate of the bromides obtained melted at 113–114°. This, with the iodine number, indicates that oleic acid and linolic acid are the two acids present. The percentage composition of the unsaturated acids calculated from the iodine number (145.0) is oleic acid, 39.9%, and linolic acid, 60.1%. These results, calculated to percentage of glycerides in the oil, give 37.41% of oleic acid glyceride and 56.37% of linolic acid glyceride. The molecular weight of the unsaturated acids (280.5) would indicate such a mixture; this was obtained by heating the acids with an excess of alkali and then titrating the excess. The usual method of direct titration gave results much higher (300.5). Repeated attempts to isolate the unsaturated acids under conditions that would eliminate oxidation or polymerization always led to the same results. This has been observed by others.⁷

Saturated Acids

Due to the small amount of saturated acids in the oil (4.86%) we were unable to obtain a quantity large enough to warrant an extended separation by fractional distillation of the methyl esters. The molecular weight by titration was 279.3; m. p. 52–53°. This would indicate that stearic acid was the chief acid present. By repeated fractional crystallization from alcohol a very small top fraction was obtained, melting at 76–77°, showing the presence of arachidic acid. The next fraction melted at 58–60° and had a molecular weight by titration of 275.7. A mixture of 40% palmitic acid and 60% stearic acid would give these results. The lower fractions did not vary much from the second fraction. Although these data are incomplete they do indicate that stearic acid and palmitic acid are the main components of the saturated acids and that arachidic acid is present in small amounts.

Unaponifiable Material

This material which was obtained in small amounts was subjected to an extended fractional crystallization. A very small phytosterol fraction was finally obtained which had a constant melting point of 165–166°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.47; H, 11.61.

Summary

Approximate analysis of the seeds and pods of the Kentucky coffee nut tree has been made. The physical and chemical characteristics of

⁶ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Co., London, 1913, 5th ed., vol. 1, pp. 568–578.

⁷ Ref. 5, pp. 517–521.

the oil from the seeds have been determined and a phytosterol having a melting point of 165–166° has been isolated. A study of the composition of the oil from the seeds has been made, the results of which are given in the following table.

COMPOSITION OF KENTUCKY COFFEE NUT TREE SEED OIL

Glycerides of	
Oleic acid, %	37.41
Linolic acid, %	56.37
Saturated acids (probably stearic and palmitic acids with a small amount of arachidic acid)	5.08
Unsaponifiable material	1.28

LEXINGTON, KENTUCKY

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

SOME PSEUDO-THIOHYDANTOINS AND ALPHA-MERCAPTO ACIDS FROM HIGHER FATTY ACIDS

BY BEN H. NICOLET AND LANGSTON FAIRCHILD BATE¹

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α -Halogeno derivatives of the simpler fatty acids or their esters condense readily with thio-urea to give 5-substituted pseudo-thiohydantoins. Acids of longer chain than butyric do not seem to have been used for this reaction, and it was thought worth while to extend it to some of the higher homologs, primarily with the hope that the derivatives might be of service in the separation or identification of the higher fatty acids.

Caproic,² lauric, myristic, palmitic and stearic acids were converted by standard methods into the α -bromo acids or esters (these react equally well). When the products, dissolved in five parts of alcohol, were warmed for an hour on the water-bath with slightly more than one molecular equivalent of thio-urea, practically quantitative yields of the crude pseudo-thiohydantoins were obtained. Several crystallizations from alcohol were usually necessary before a constant melting point was reached. The results are summarized in Table I.

TABLE I
PSEUDO-THIOHYDANTOINS

Description	M. p., °C.	Formula	N, %		Soluble in 100 cc. of 95% alc. at 25°, g.
			Calcd.	Found	
5-Butyl-	183	C ₇ H ₁₂ ON ₂ S	16.27	16.38, 16.25	...
5-Decyl-	182.5	C ₁₃ H ₂₄ ON ₂ S	10.93	11.08, 11.10	0.452
5-Dodecyl-	180.5	C ₁₅ H ₂₈ ON ₂ S	9.75	9.83, 9.91	.267
5-Tetradecyl-	176.5	C ₁₇ H ₃₂ ON ₂ S	8.96	8.97, 9.01	.082
5-Hexadecyl-	175	C ₁₉ H ₃₆ ON ₂ S	8.23	8.33, 8.37	.007

¹ The material here presented is from the Doctor's Dissertation of Langston Fairchild Bate, University of Chicago, August, 1926.

² The work on caproic acid was done by Mr. Sik-Chew Lui.

While the substances obtained are easily formed in excellent yields, they are not at all suitable for the intended use, as they show little or no melting-point depression when mixed, and thus presumably form solid solutions to an unusual extent. A similar product prepared from commercial "stearic acid," containing about equimolecular proportions of palmitic and stearic acids, melted at 175° . It is to be noted that the melting points obtained for the various members of the series are rather close together, and tend to fall as the length of the side chain increases.

As their structure suggests, these pseudo-thiohydantoin can be hydrolyzed to give the corresponding mercapto acids. The method adopted after several trials was to boil a solution of the hydantoin with an equal weight of sodium hydroxide in 10 parts of 85% alcohol. The hydrolysis usually required about 20 hours. At the end of this time, the solution was diluted and acidified, and the acid which separated was decolorized and crystallized from alcohol. The data are summarized in Table II.

TABLE II
 α -MERCAPTO ACIDS

Description	M. p., $^{\circ}\text{C}$.	Formula	Calcd.		Found	
			S, %	Equiv. wt.	S, % ^a	Equiv. wt. ^b
Caproic ^c	b. 234	$\text{C}_6\text{H}_{12}\text{O}_2\text{S}$		148.1		148.2
Lauric	59	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	13.8	232.2	13.65 13.71	233
Myristic	66	$\text{C}_{14}\text{H}_{28}\text{O}_2\text{S}$	12.31	260.2	12.42 12.44	259.7
Palmitic	72-73	$\text{C}_{16}\text{H}_{32}\text{O}_2\text{S}$	11.12	288.3	10.81 10.71	290
Stearic	80	$\text{C}_{18}\text{H}_{36}\text{O}_2\text{S}$	10.13	316.3	10.27 10.32	316

^a Carius method.

^b By titration in alcohol.

^c The α -mercaptocaproic acid was prepared by hydrolysis with barium hydroxide in much more dilute alcohol and isolated as the barium salt, which was readily soluble in water and melted at 192° .

Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_4\text{S}_2\text{Ba}$: Ba, 31.8. Found: 31.74, 31.88.

The relative ease of oxidation of mercaptans to the corresponding disulfides makes it difficult to predict whether products obtained by the procedure described would be the mercapto acids or their oxidation products. The sulfur content and the equivalent weight are scarcely sufficient to decide this question. Accordingly, the substance described as mercapto-lauric acid was dissolved in acetic acid containing sodium acetate in excess, and one equivalent of iodine, also in acetic acid, was added to the warm solution. The iodine was reduced, and from the solution lauric acid α -disulfide was obtained, melting at 48° .

Anal. (Carius). Calcd. for $\text{C}_{14}\text{H}_{28}\text{O}_4\text{S}_2$: S, 13.86. Found: 13.61, 13.55. Equiv. wt. Calcd. (dibasic): 231.3. Found: 233.

The original product was thus evidently the mercapto acid.

A number of the simpler pseudo-thiohydantoins have been oxidized to the corresponding sulfonic acids, usually with potassium chlorate and hydrochloric acid in water solution. This method seemed of doubtful applicability to such insoluble substances as those described in this paper. A number of attempts under rather varied conditions were made to obtain the sulfonic acids in question by oxidation of the mercapto acids, but no products of even approximate purity were isolated except in the case of mercaptocaproic acid.

α -Carboxy-*n*-amylsulfonic Acid.—Barium mercaptocaproate was oxidized in water solution with the calculated amount of barium permanganate. The barium salt of the sulfonic acid was readily soluble in hot water, and melted at 196°.

Anal. Calcd. for $C_6H_{10}O_6S\text{Ba}$: Ba, 41.43. Found: 41.31.

The free sulfonic acid could not be obtained crystalline.

Summary

1. The pseudo-thiohydantoins corresponding to caproic, lauric, myristic, palmitic and stearic acids have been described, together with the α -mercapto acids obtained from them by hydrolysis.

2. The pseudo-thiohydantoins, while easily obtainable, offer no promise as derivatives for the separation or identification of the higher fatty acids.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

A SUGGESTED MECHANISM OF THE SPLITTING OF THE CYCLOPROPANE RING BY BROMINE

BY BEN H. NICOLET AND LOUIS SATTLER¹

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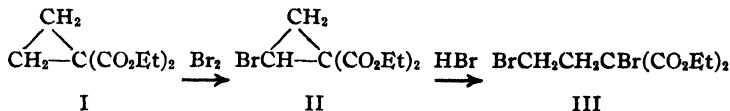
The splitting that occurs when bromine acts on cyclopropane derivatives has usually been considered to take place by the addition of bromine at the bond broken. Cyclopropane carboxylic acid, for example, gives with bromine both the 1-bromo-substitution product and α,γ -dibromobutyric acid. It seems customary to regard these two substances as products of simultaneous and independent reactions.² Bruylants³ remarks that in

¹ The material here presented was used by Louis Sattler in partial satisfaction of the requirements for the degree of Doctor of Philosophy, University of Chicago, 1925.

² After this paper had been prepared for publication, a translation of a rather inaccessible article by Kischner [*J. Russ. Phys.-Chem. Soc.*, **41**, 659 (1909)] was obtained. Kischner remarks: "The described results of the bromination of the chloride of trimethylene carboxylic acid, as well as of the acid itself, may be formulated as the addition of one molecule of bromine. It might be more accurate, however, to describe the production of the end product as the result of two successive stages: (a) the formation of the normal substitution product; (b) the addition of hydrogen bromide, which is accompanied by the rupture of the trimethylene ring." He did not test the action of

this case substitution seems to be "an altogether subordinate reaction."

We have studied the action of bromine on diethyl cyclopropane-1,1-dicarboxylate (I) and found that two products can be isolated, the 2-bromo derivative (II) and β -bromoethyl-bromomalononic ester (III).



When the bromination was carried out at 40–50°, using a powerful quartz-mercury vapor lamp as light source, more II was isolated than when the reaction took place at a higher temperature, with or without illumination. The separation of II and III by fractionation under reduced pressure is tedious, but after four or five distillations moderately pure products were obtained.

The structure of III follows from its reaction with zinc in dil. alcohol; cyclopropane-1,1-dicarboxylic acid was identified. After hydrolysis, III was converted into the phenylhydrazide of α,γ -dihydroxybutyric acid (IV), which was identical with a sample previously obtained in another way.⁴

When II was warmed for nine hours with 80% hydrobromic acid, and the resulting product (presumably α,γ -dibromobutyric acid) hydrolyzed by shaking with silver oxide, the same phenylhydrazide (IV) could be isolated. It was shown to be identical with the other preparations mentioned. It is therefore assumed that hydrogen bromide splits II in such a way as to give III. The formation of IV in this way is evidence for the structure assigned to II, and rules out the alternative possibility that II might be $\text{BrCH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$. This conclusion is confirmed by the fact that the bromine of II is very difficult to remove by hydrolysis.

It is believed that the formation of the dibromide III from the bromo-derivative II has been definitely demonstrated. This result is somewhat surprising, as there was perhaps more reason for expecting the formation of $\text{Br}_2\text{CHCH}_2\text{CH}(\text{CO}_2\text{Et})_2$ in such a reaction. This is, so far as we know, the first case in which the product obtained by the splitting of a bromo-cyclopropane derivative with hydrogen bromide has been determined. The chief interest in the result, however, lies in the identity of the product formed from II and hydrogen bromide with the one to be expected if bromine had added directly to I. The suggestion is obvious that much or all of the III obtained by the action of bromine on I, was formed through II hydrogen bromide on 1-bromocyclopropane-1-carboxylic acid, and assumed such an action as possible only because it involved addition of the bromine (of hydrogen bromide) to the carbon *not* attached to carboxyl.

³ Bruylants, *Bull. soc. chim. Belg.*, **32**, 358 (1923).

⁴ Glattfeld and Sander, *This Journal*, **43**, 2675 (1921). A sample for comparison was kindly supplied by Dr. Glattfeld.

as an intermediate. While it remains possible that III may also be formed directly from I by bromine addition, the evidence for this latter reaction is distinctly less definite. The suggestion is made that the normal action of bromine on the cyclopropane ring may well be not the addition of bromine, but substitution, followed by addition of hydrogen bromide.

There is, of course, no compelling reason why the subsequent addition of hydrogen bromide should always result in the breaking of one of the two bonds adjacent to the carbon carrying the bromine. In fact, Gustavson⁵ found that bromine gave with 1,1-dimethyl cyclopropane, $\text{Me}_2\text{CBrCHBrCH}_3$, a product not derivable by direct bromine addition. He assumed that traces of hydrogen bromide first caused ring splitting to yield Me_2CBrEt , which then underwent bromination to give the observed product, at the same time supplying the hydrogen bromide necessary for the first stage of the reaction. The mechanism he has suggested could not apply to the case discussed in this paper. To settle the question, other monobromo-derivatives of cyclopropane isolated in brominations will have to be heated with hydrogen bromide to see whether the dibromo-compounds obtained are the same as those resulting from "direct" bromination.

The action of bromine on cyclopropylcyanide, 1-cyanocyclopropane-1-carboxylic acid, cyclopropane-1,1-dicarboxylic acid, and ethyl 1-cyanocyclopropane-1-carboxylate is described in the experimental part.

In a further attempt to find reactions in which addition might take place with splitting of the cyclopropane ring, the action of HOCl and HOBr in water solution and that of ICl in glacial acetic acid, were tried on 1-cyanocyclopropane-1-carboxylic acid and on cyclopropane-1,1-dicarboxylic acid. There was no evidence of reaction in any case.

Experimental Part

Preparation of Required Cyclopropane Derivatives.—Ethyl cyclopropane-1,1-dicarboxylate was prepared by the method of Dox and Yoder⁶ with slight modifications. The yield obtained was consistently about 75% of that given by the authors mentioned. The corresponding acid was isolated as described by Stohmann and Kleber.⁷ The yields were decidedly poor. For ethyl 1-cyanocyclopropane-1-carboxylate, the method of Jones and Scott⁸ was used. For 1-cyanocyclopropane, the method of Haller and Benoist⁹ was modified. A 15% excess of potassium hydroxide¹⁰ was pulverized and

⁵ Gustavson, *J. prakt. Chem.*, [2] 62, 270 (1900).

⁶ Dox and Yoder, *THIS JOURNAL*, 43, 2097 (1921).

⁷ Stohmann and Kleber, *J. prakt. Chem.*, [2] 45, 477 (1892).

⁸ Jones and Scott, *THIS JOURNAL*, 44, 413 (1922).

⁹ Haller and Benoist, *Ann. chim.*, [9] 17, 28 (1922); little detail is given, but results are surely much less good than the text implies.

¹⁰ Potassium hydroxide was fused for 10 minutes in a silver crucible at about 300°, and poured into warmed test-tubes which were promptly stoppered and placed in a desiccator. This product could be ground effectively as required.

placed in a 100cc. distilling flask fitted with a rather fine capillary and a dropping funnel. The flask was attached to a pump and heated (without fusing the potassium hydroxide) to remove some of the water which had been absorbed during grinding. When the flask had cooled, it was attached, through a condenser and receiver, to the pump, placed in a water-bath at 85°, and γ -chlorobutyronitrile (32 g.) allowed to run in slowly. The reaction should take place rapidly, and the product be removed by distillation as promptly as possible. To obtain a halogen-free product, the distillate was again treated similarly with potassium hydroxide. The yield was 8–11 g. (40–55%) of cyanocyclopropane, boiling at 134°.

Action of Bromine on Ethyl Cyclopropane-1,1-dicarboxylate (I).—Bromine reacts easily with I, even in diffused light. The nature of the product depends on the conditions of bromination. Apparently, both ethyl 2-bromocyclopropane-1,1-dicarboxylate (II) and ethyl β -bromo-ethyl-bromomalonate (III) are formed in each case, but the proportion of the latter was much larger when bromination was carried out at higher temperatures, and with illumination by a mercury arc.

I, preheated to 50°, was treated slowly with 1 mole of bromine in the presence of the arc. The reaction rate increased as hydrobromic acid accumulated and as the solution became warmer. Unless considerable care was taken, the reaction finally became quite violent. On distillation, a typical product (23 g.) gave, in addition to lower-boiling material, (a) 9 g. b_{15} 150–160° and (b) 6 g. b_{15} 160–165°; both fractions consisted chiefly of III.

Anal. Calcd. for $C_6H_{14}O_4Br_2$: C, 31.22; H, 4.07. Found: (a) C, 31.70; H, 4.35. (b) C, 30.91; H, 4.27.

The best sample of III prepared boiled under 10 mm. pressure at 146–151°.

A larger portion of the monobromo derivative (II) was formed when 155 g. of I was placed in a flask attached to a reflux condenser and cooled in an ice-bath while 1 mole of bromine was added during two hours. No special illumination was used. The reaction appeared to be decidedly autocatalytic. After five careful fractionations at pressures of 10–17 mm., II and III were not completely separated.

Anal. Calcd. for $C_6H_{12}O_4Br$: Br, 30.17. Calcd. for $C_6H_{14}O_4Br_2$: Br, 46.20. Found: (a) b_{15} 135–140°; Br, 31.8. (b) b_{15} 140–145°; Br, 32.6, 32.3. (c) b_{10} 146–151°; Br, 45.0.

Formation of Cyclopropane-1,1-dicarboxylic Acid from III. Four g. of an analyzed sample of III was boiled under reflux for five hours with an excess of zinc dust. The solution was then diluted with water, filtered from undissolved zinc, and boiled for some time with excess potassium hydroxide to saponify the ester. From the acidified solution, cyclopropane-1,1-dicarboxylic acid was extracted with ether and recrystallized from chloroform. Three-tenths g. (20%) of the pure acid was obtained. It had the correct melting point, which was not lowered by mixture with a known sample.

Preparation of the Phenylhydrazide of α,γ -Dihydroxybutyric Acid from β -Bromo-ethyl-bromomalonate Ester.—Ten g. of a fraction of the ester III b_{15} 150–155° was refluxed with constant-boiling hydrobromic acid until solution was complete, and the ester presumably converted to α,γ -dibromobutyric acid. Excess hydrobromic acid was removed by distillation at 14 mm. The residue was dissolved in 200 cc. of water, an excess of freshly precipitated silver oxide added, and the mixture shaken for 18 hours in a machine. After filtration, the residue was again shaken with water for some time, and the extract added to the filtrate mentioned. The resulting solutions were concentrated under reduced pressure, the organic material taken up in alcohol, and an excess of phenylhydrazine added. The crystals obtained were purified from ethyl acetate. The yield of pure hydrazide was 1.9 g. (31%); m. p., 129.5°. Mixture with a known sample of the product⁴ did not change the melting point.

Preparation of the Phenylhydrazide of α,γ -Dihydroxybutyric Acid from Diethyl 2-Bromocyclopropane-1,1-dicarboxylate.—Five g. of a fraction b_{11} 135–140° of the ester II, estimated by analysis as 97% pure, was warmed (without boiling) for four hours with 20 g. of 80% hydrobromic acid, and then refluxed for five hours more. After the removal of water and hydrobromic acid by distillation under reduced pressure, the residue, assumed to be α,γ -dibromobutyric acid, boiled at 130–131° under 15 mm. By a procedure similar to that described in the preceding paragraph, this was hydrolyzed with silver oxide, treated with phenylhydrazine, and a phenylhydrazide of α,γ -dihydroxybutyric acid obtained, identical by all tests with that described above.

Action of Bromine on Cyanocyclopropane and on 1-Cyanocyclopropane-1-carboxylic Acid.—After several hours' exposure to the light of a quartz-mercury vapor lamp, almost no bromine had reacted and the products were recovered practically unaltered.

Action of Bromine on Cyclopropane-1,1-dicarboxylic Acid.—Under the influence of ultraviolet light, the action of bromine on this acid is slow, but is completed in three to four hours. In CCl_4 , the product was β -bromo-ethyl-bromomalonic acid,¹¹ of which 2.7 g. (76%) was isolated, melting at 111° and evolving carbon dioxide at 113°. The ammonium salt was precipitated from dry ether.

Anal. (Kjeldahl). Calcd. for $\text{C}_4\text{H}_8\text{O}_4\text{N}_2\text{Br}_2$: N, 8.66. Found: 8.68.

A similar bromination, with chloroform as solvent, took a different course. The product was a very viscous oil. On distillation at 20 mm. it lost carbon dioxide and gave a thick oil, boiling at 140° under 20 mm., which did not solidify at –14°. This was apparently 2-bromocyclopropane-1-carboxylic acid.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{O}_2\text{Br}$: C, 29.09; H, 3.64. Found: C, 29.37; H, 3.57.

Action of Bromine on Ethyl 1-Cyanocyclopropane-1-carboxylate.—This ester behaves with bromine much as does I. Near its boiling point, it reacted vigorously with slowly added bromine and much hydrobromic acid was evolved. Two products, ethyl 2-bromo-1-cyanocyclopropane-1-carboxylate and ethyl α,γ -dibromo- α -cyano-acetate (V), were apparently formed, but a complete separation proved too tedious. After two careful fractionations at 11 mm. pressure, the following analyses were obtained.

Anal. (Carius). Calcd. for $\text{C}_7\text{H}_9\text{O}_2\text{NBr}$: Br, 36.7. Calcd. for $\text{C}_7\text{H}_9\text{O}_2\text{NBr}_2$: Br, 53.7. Found: (a) b_{11} 100–105°, Br, 45.8. (b) b_{11} 136–140°, Br, 52.6.

The latter fraction was apparently moderately pure V.

Action of HOCl and HOBr on Cyclopropane-1,1-dicarboxylic Acid and on 1-Cyanocyclopropane-1-carboxylic Acid.—The acid to be tested was dissolved in alkali and treated with a solution containing 1 mole of NaOCl or NaOBr. The solution was then cooled below 0°, carbon dioxide passed in to liberate the hypohalous acid, and the solution allowed to stand for some time (occasionally up to two days in the ice box). There was no evidence of reaction, and the unaltered acid was recovered in each case.

Action of ICl on Cyclopropane-1,1-dicarboxylic Acid and on 1-Cyanocyclopropane-1,1-carboxylic Acid.—Each acid was treated with 1 mole of ICl in glacial acetic acid solution, and the mixture allowed to stand for periods up to three weeks. There was no evidence of reaction, and titration showed a negligible decrease in the amount of ICl present. Even in ultraviolet light, no reaction could be detected.

Summary

1. Some new derivatives of cyclopropane have been described.
2. In the bromination of diethyl cyclopropane-1,1-dicarboxylate, the 2-bromo-derivative was isolated and shown to react with hydrobromic acid

¹¹ Marburg, *Ann.*, 294, 125 (1897).

to give β -bromo-ethyl-bromomalonic ester. It is suggested that substitution, followed by splitting of the ring with addition of hydrobromic acid, may be the normal mechanism of the breaking of the cyclopropane ring by bromine.

3. A number of cyclopropane derivatives showed no reaction with HOCl, HOBr or ICl.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE ADDITION OF ETHYL AND TERTIARY BUTYL HYPOCHLORITES TO CINNAMIC ACID

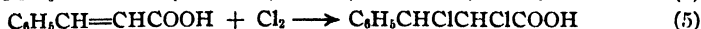
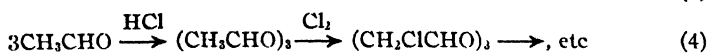
BY ERNEST L. JACKSON AND L. PASIUT

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The addition of methyl hypochlorite to cinnamic acid and other ethylene derivatives, by the reaction of chlorine with the unsaturated compounds in methyl alcohol solution, was reported in a previous paper.¹ The question of the applicability of this reaction to other alcohols led to the investigation of ethyl and *tert.*-butyl alcohols, the results of which are given in this paper.

Chattaway and Backeberg² have recently shown that in the chlorination of ethyl alcohol, ethyl hypochlorite and hydrogen chloride are the primary products and that in the presence of unchanged alcohol the ethyl hypochlorite quickly eliminates hydrogen chloride from its molecule with the formation of acetaldehyde, the chlorination of which follows. One would expect, therefore, the addition of ethyl hypochlorite to cinnamic acid, by the reaction of chlorine with the unsaturated compound in ethyl alcohol solution, to be complicated by a number of side reactions. The principal reactions follow.



By introducing a slow stream of dry chlorine into an efficiently stirred solution of cinnamic acid in absolute ethyl alcohol, we were able to add ethyl hypochlorite to the double linkage of the unsaturated compound. The chlorine concentration was kept as low as practicable and the temperature was either that of the Laboratory, or 0–10°, the results being about the same in both cases. Most of the chlorine went into the side

¹ Jackson, *THIS JOURNAL*, **48**, 2166 (1926).

² Chattaway and Backeberg, *J. Chem. Soc.*, **125**, 1097 (1924).

reactions, about three times the calculated amount being required to complete the reaction and large quantities of aldehyde being evident in the chlorinated mixture. The products, which were isolated by saponification of the esters resulting from the chlorination, were α -chloro- β -ethoxyphenylpropionic acid, α -chlorocinnamic acid, and α -chloro- β -hydroxyphenylpropionic acid, while the presence of allocinnamic acid was strongly indicated. The yield of the chloro-ethoxy acid was low (about 6%). The α -chloro- β -hydroxyphenylpropionic acid was formed by the addition of hypochlorous acid to cinnamic acid, while α -chlorocinnamic acid was doubtless produced by the action of sodium hydroxide with ethyl α - β -dichloro- β -phenylpropionate during the saponification reaction.³ The reaction of chlorine with an alcoholic solution of ethyl cinnamate was found to give a somewhat higher yield (10%) of the chloro-ethoxy acid.

A number of experiments with alcoholic solutions of cinnamic acid were tried with a view to improving the yield of the chloro-ethoxy acid by eliminating the hydrochloric acid formed in the reaction. Oxidation of the hydrochloric acid by means of potassium chlorate gave a 9% yield of the chloro-ethoxy acid, while 22% of the cinnamic acid was converted into α -chloro- β -hydroxyphenylpropionic acid. Although the yield of the chloro-ethoxy acid was not materially improved by this method, the amount of chlorine required was only one-third that necessary in the absence of potassium chlorate. When calcium carbonate was suspended in the reaction solution, we could isolate only α -chloro- β -hydroxyphenylpropionic acid. With the use of pyridine and the calculated amount of chlorine, 80% of the cinnamic acid was recovered unchanged. On the basis of the equation $C_2H_5ONa + Cl_2 \rightarrow C_2H_5OCl + NaCl$, we tried without success the reaction of the calculated amount of chlorine with a suspension of sodium cinnamate in an absolute alcohol solution of sodium ethylate.

Inasmuch as Goldschmidt⁴ has shown that the addition of ethyl hypochlorite to 1,4-dihydronaphthalene may be accomplished in carbon tetrachloride solution, we hoped to utilize this method for the addition of ethyl hypochlorite to cinnamic acid. It was found, however, that cinnamic acid failed to react with ethyl hypochlorite in carbon tetrachloride, a pure, dry solution of which was prepared by the procedure of Taylor, MacMullin and Gammal,⁵ although tests showed the presence of ethyl hypochlorite in the solution during three days.

The stability of *tert.*-butyl hypochlorite^{5,6} led to the hope that chlorina-

³ Sudborough and James, *J. Chem. Soc.*, **89**, 105 (1906).

⁴ Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).

⁵ Taylor, MacMullin and Gammal, *THIS JOURNAL*, **47**, 395 (1925).

⁶ Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

tion of a solution of cinnamic acid in *tert.*-butyl alcohol would result in a more satisfactory addition of the hypochlorite than was obtained in the case of ethyl hypochlorite, where the rate of decomposition apparently exceeds the rate of the addition reaction. We found, in fact, that *tert.*-butyl hypochlorite may be readily added to cinnamic acid in this manner, although only a 14% yield of pure α -chloro- β -*tert.*-butoxy-phenylpropionic acid results. It was necessary to use almost three times the calculated amount of chlorine, because of side reactions between chlorine and *tert.*-butyl alcohol.

(The principal reaction between *tert.*-butyl alcohol and chlorine seems to be substitution of the hydrogen in the methyl groups.⁷ On the basis of the facts at present available, it is not possible to state whether the *tert.*-butyl hypochlorite formed in our reaction is a result of the direct action of chlorine with the alcohol, or is formed by the action of the alcohol with hypochlorous acid, which might result from the reaction of chlorine with small amounts of water present in the alcohol.)

Although the addition of *tert.*-butyl hypochlorite to benzalacetophenone, by its reaction with chlorine and *tert.*-butyl alcohol, could not be established, we were able to isolate a stereo-isomer of α,β -dichloro- β -phenylpropionophenone, which has hitherto not been reported. The new isomer melts at 82–83° and is more soluble in alcohol than the high-melting isomer (113°). That the substance is a stereo-isomer of benzalacetophenone dichloride, and not a structural isomer, was established by its reaction with hydroxylamine to give diphenylisoxazole, which Goldschmidt⁸ has shown to be the product of this reaction with the high-melting dichloride.

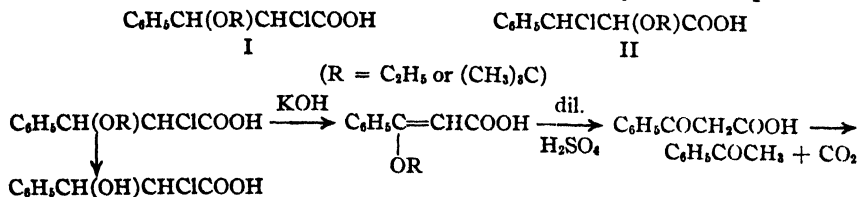
The Mode of Addition

In the addition of methyl hypochlorite to cinnamic acid, the chlorine atom has been shown¹ to go exclusively to the carbon atom in the alpha position to the carboxyl group, while the methoxyl radical combines with the carbon in the beta position. This result is analogous to the well-known mode of addition of hypochlorous acid, the methoxyl and hydroxyl groups assuming the same position in the addition product. We found, likewise, that in the addition of ethyl and *tert.*-butyl hypochlorites to cinnamic acid, the chlorine combines with the alpha carbon while the alkoxyl group attaches itself to the beta carbon. Our evidence for the structure of the ethyl and *tert.*-butyl hypochlorite addition products is based upon the preparation of acetophenone by their reaction with alcoholic potassium hydroxide, followed by hydrolysis of the resulting oils with dil. sulfuric acid solution. In the case of the *tert.*-butyl hypochlorite addition product, both acetophenone and α -chloro- β -hydroxyphenyl-

⁷ Davis and Murray, *Ind. Eng. Chem.*, **18**, 845 (1926).

⁸ Goldschmidt, *Ber.*, **28**, 2540 (1895).

propionic acid were obtained by this treatment. The formation of acetophenone and α -chloro- β -hydroxyphenylpropionic acid from the α -chloro- β -alkoxy acid (I) is readily explained as shown by the equations below, while the β -chloro acids (II) would not be expected to yield these products.



Although the unsaturated alkoxy acids resulting from the reaction with alcoholic potassium hydroxide were not isolated, the oils thus obtained were shown to decolorize bromine in carbon tetrachloride solution and to reduce potassium permanganate rapidly in sodium carbonate solution. Perkin⁹ has shown that benzoylacetic acid, on heating with dil. sulfuric acid solution, is quantitatively decomposed into acetophenone and carbon dioxide. One would expect, therefore, our treatment of the product, resulting from the reaction with alcoholic potassium hydroxide, with dil. sulfuric acid solution and steam to yield acetophenone. The formation of α -chloro- β -hydroxyphenylpropionic acid in the reactions with the *tert.*-butyl hypochlorite addition product was doubtless due to hydrolysis of some of the chloro-*tert.*-butyloxy acid.

Experimental Part

Addition of Ethyl Hypochlorite

The ethyl alcohol used in this work was refluxed over quicklime and distilled through a fractionating column. With the exception indicated, the temperature of the experiments was that of the Laboratory.

Reaction of Cinnamic Acid with Chlorine and Absolute Ethyl Alcohol.—Twenty g. of cinnamic acid was dissolved in 100 cc. of absolute ethyl alcohol. A slow stream of chlorine, dried by bubbling through concd. sulfuric acid, was introduced into the vigorously stirred solution. The concentration of chlorine was kept as low as possible, so that several hours were required to complete the reaction. A number of experiments showed that approximately 9 liters of chlorine (about thrice the calculated amount) gave the best results with 20 g. of cinnamic acid. Upon completion of the chlorination the solvent, which had a strong aldehyde odor, was distilled under diminished pressure. The residue was an oil, nearly all of which (20.5 g.) boiled at 122–124° (5 mm.). This material, a mixture of acid esters, was boiled with a small excess of 0.5 *N* sodium hydroxide solution until saponification was complete. The chlorostyrene, formed by the reaction of sodium hydroxide with the dichloride of cinnamic acid, was extracted with ether. Acidification of the alkaline solution precipitated an oil which slowly crystallized. The crystals were filtered off and dried. Recrystallization from benzene gave 2 g. of substance melting at 134–138° and an oil. On further recrystallization of the

⁹ Perkin, *J. Chem. Soc.*, 45, 178 (1884).

substance melting at 134–138° long, transparent needles melting at 137–138° were obtained. The oil crystallized only after long standing. Suction filtration of the sirupy material thus obtained yielded 2 g. of colorless crystals melting at 69–78°, which after several recrystallizations from benzene melted at 78–79°. The oily filtrate from the substance melting at 69–78° was suspended in dil. aqueous sodium hydroxide and boiled until solution was complete and the odor of chlorostyrene was no longer perceptible. Acidification of this solution precipitated an oil, which crystallized on standing; m. p., 57–61°. The substance in dil. sodium carbonate solution rapidly decolorizes aqueous potassium permanganate at room temperature, producing the odor of benzaldehyde. It probably consists chiefly of allocinnamic and isocinnamic acids. In one experiment, by oxidation of this material with potassium permanganate solution and acidification of the resulting solution, there was obtained a small amount of α -chloro- β -hydroxyphenylpropionic acid; m. p., 79–81°. A mixture with the known acid melted at the same temperature.

The crystals melting at 137–138° were shown to be α -chlorocinnamic acid, which was doubtless formed by the reaction of aqueous sodium hydroxide with ethyl α,β -dichloro- β -phenylpropionate during the saponification described above.

Anal. Calcd. for $C_9H_7O_2Cl$: Cl, 19.42. Found: 19.35.

No depression of the melting point was produced on mixing with known α -chlorocinnamic acid; m. p., 137–138°. Also, the melting point of the acid amide, 120–121°, prepared by the procedure of Stoermer,¹⁰ corresponds with that of the acid amide of α -chlorocinnamic acid.

The substance melting at 78–79°, obtained as described above, is α -chloro- β -ethoxyphenylpropionic acid containing one molecule of crystal water. The water of crystallization was determined by heating to constant weight at 115°; the ethoxyl analysis was made by the Zeisel method.

Anal. Calcd. for $C_{11}H_{13}O_3Cl \cdot H_2O$: H_2O , 7.31; OC_2H_5 , 18.26; Cl, 14.37. Found: H_2O , 7.50; OC_2H_5 , 18.26; Cl, 14.21.

By chlorinating a solution of 10 g. of cinnamic acid in 50 cc. of absolute ethyl alcohol cooled in ice water, the yield of the chloro-ethoxy acid was 1 g. (6%).

Structure of the Chloro-ethoxy Acid.—The sample used in the following experiment was shown by an ethoxyl determination to contain 87% of the chloro-ethoxy acid. One and one-half g. of this substance, melting at 77–79°, was added to a solution of 2.4 g. of potassium hydroxide in 13 cc. of absolute alcohol. After boiling under a reflux condenser for six hours, the alcohol was distilled, the residue dissolved in water and acidified, the oil thus precipitated being extracted with ether. To the oil obtained by distillation of the ether there was added 100 cc. of 10% aqueous sulfuric acid; this mixture was then steam distilled until oily material ceased to pass over. From the distillate there was obtained by extraction with ether 0.6 g. of oil which resembled acetophenone in appearance and odor. In order to identify the substance, the semicarbazone was prepared by the reaction of the oil with semicarbazide hydrochloride and sodium acetate according to the usual procedure; m. p., 195–196°; yield, 0.6 g., which corresponds to an amount of acetophenone equal to 65% of the calculated amount, on the basis of a quantitative conversion of the chloro-ethoxy acid into acetophenone. The melting point of the substance showed no depression when mixed with known acetophenone semicarbazone; m. p., 195–196°. From the aqueous solution left in the distilling flask in the steam distillation described above, there was obtained by extraction with ether about 0.1 g. of an oil which was not investigated. Since the formation of acetophenone by these reactions is most logically explained on the assumption that the ethoxyl group is in the

¹⁰ Stoermer, *Ber.*, **44**, 647 (1911).

beta position to the carboxyl group, it is concluded that the substance is α -chloro- β -ethoxyphenylpropionic acid.

Reaction with Ethyl Cinnamate.—A solution of 29 g. of ethyl cinnamate in 100 cc. of absolute ethyl alcohol was treated with 10 l. of chlorine in the manner described above. At the end of the reaction the product was heated with dil. sodium hydroxide solution until saponification of the esters was complete. After extracting the chloro-styrene thus formed, the solution was acidified and an oil precipitated. This on standing partially crystallized. By means of a fractional crystallization from benzene, there were obtained 4 g. of α -chlorocinnamic acid melting at 135–138°, 3 g. of substance melting at 50–105° and 8 g. of oil containing some crystals. By allowing the 8 g. of sirupy material to stand for about three weeks, there were separated with the aid of benzene 4 g. of α -chloro- β -ethoxyphenylpropionic acid melting at 78–80° (10% yield). An ethoxyl determination showed the substance to contain 89% of the chloro-ethoxy acid.

Reaction of Cinnamic Acid with Chlorine and Ethyl Alcohol in the Presence of Calcium Carbonate.—Into a thoroughly stirred suspension of 10 g. of cinnamic acid and 20 g. of finely powdered calcium carbonate in 55 cc. of absolute ethyl alcohol, there was introduced about 4.5 liters of chlorine at such a rate as to maintain only a slight excess. The reaction mixture was then diluted with water and acidified, an oil being precipitated. The oil crystallized on standing; m. p., 60–75°; wt., 7 g. By recrystallization from benzene this material was separated into hydrated α -chloro- β -hydroxyphenylpropionic acid melting at 79–81° (4.5 g.) and 1.5 g. of substance melting at 50–70°, which probably consists chiefly of the low-melting isomers of cinnamic acid. The substance melting at 79–81° is easily soluble in hot water, from which it crystallizes in long needles. A qualitative test by the Zeisel method showed that it contained no ethoxyl group.

Anal. Calcd. for $C_9H_8O_3Cl \cdot H_2O$: Cl, 16.22. Found: 15.61.

Its identity was confirmed by converting it into α -chlorocinnamic acid by reaction with acetic anhydride and sodium acetate,¹¹ and by the preparation of α,β -dichloro- β -phenylpropionic acid by heating it in a sealed tube with fuming hydrochloric acid.

Reaction in the Presence of Potassium Chlorate.—A vigorously stirred suspension of 20 g. of cinnamic acid and 2.6 g. of potassium chlorate in 100 cc. of absolute ethyl alcohol was treated with 3 liters of chlorine (one molecular equivalent) at the rate of about one bubble per second, seven hours being required to complete the reaction. Qualitative tests showed that the solid, suspended in the solution at the end of the reaction, was a mixture of potassium chloride and potassium chlorate. After the chlorination had been completed, the solution was poured into about 1000 cc. of water. The oil, thus precipitated, partially crystallized on standing for about 24 hours. The oily material was separated from the solid by suction filtration. The solid thus obtained weighed 9 g. and melted at 60–77°. By recrystallization from benzene 6.5 g. of hydrated α -chloro- β -hydroxyphenylpropionic acid was obtained; m. p., 79–81°. No depression of the melting point was produced on mixing with the known acid. The oil obtained in the above described filtration was heated with 0.5 *N* sodium hydroxide solution for an hour. After extracting the insoluble material with ether, the solution was acidified, an oil being precipitated. This crystallized on standing for several hours; wt., 6 g.; m. p., 55–63°. This material contains α -chloro- β -ethoxyphenylpropionic acid mixed with the low-melting isomers of cinnamic acid. For purification it was dissolved in dil. sodium carbonate solution and treated with potassium permanganate solution in slight excess. After filtering off the manganese dioxide, extracting the benzaldehyde with ether and acidifying, an oil was precipitated which immediately crystallized. This was filtered off and air dried; wt., 1.8 g.; m. p., 68–75°. A Zeisel test showed the substance

¹¹ Forrer, *Ber.*, 16, 854 (1883).

to be an ethoxyl compound. Recrystallization from benzene gave pure α -chloro- β -ethoxyphenylpropionic acid; m. p., 78–79°. A mixture with the known acid melted at the same temperature. By extracting the filtrate from the substance melting at 68–75° with ether and distillation of the solvent, after drying over sodium sulfate, there was obtained an oil which soon crystallized. From this 1.2 g. of α -chloro- β -ethoxyphenylpropionic acid melting at 65–75° was obtained. One recrystallization from benzene gave the pure chloro-ethoxy acid; m. p., 78–79°.

Addition of Tertiary Butyl Hypochlorite

The *tert.*-butyl alcohol used was the "anhydrous" grade manufactured by the Petroleum Chemical Corporation. The commercial product was found to give about the same results as *tert.*-butanol boiling at 81–82°.

Reaction of Cinnamic Acid with Chlorine and *tert.*-Butyl Alcohol.—A vigorously stirred solution of 25 g. of cinnamic acid in 350 cc. of *tert.*-butyl alcohol was treated with a stream of dry chlorine until approximately 10.5 liters (about 2.8 times the calculated amount) had reacted. The use of less chlorine gave an incomplete reaction of the cinnamic acid because of side reactions between chlorine and *tert.*-butyl alcohol. The temperature was that of the Laboratory, and the rate of introduction of chlorine was such as to maintain only a small excess, about 15 hours being required to complete the reaction. At the end of the reaction the *tert.*-butyl alcohol was distilled under diminished pressure, the bath temperature being 60–70°. The residue was an oil, which was dissolved in ether and thoroughly extracted with saturated aqueous sodium carbonate. The small amount of insoluble material remaining in the ether was not investigated. The sodium carbonate solution was heated at the boiling point for about three minutes. This treatment decomposes cinnamic acid dichloride to give chlorostyrene, which is removed by means of ether. On acidifying the sodium carbonate solution, there precipitated an oil, which was extracted with ether. After drying and distilling the solvent, an oil was obtained. The oil showed slight tendency to crystallize upon standing and with the use of the common solvents, except benzene. It was dissolved in benzene and allowed to evaporate almost to dryness at room temperature. The crystalline mass thus obtained was separated from the oily material by means of suction filtration; m. p., 60–70°. This is principally α -chloro- β -*tert.*-butyloxyphenylpropionic acid contaminated with the low-melting isomers of cinnamic acid. The substance may be obtained completely pure by further recrystallization from benzene; however, the purification may be facilitated by oxidation of the unsaturated compounds with dil. potassium permanganate solution, which was shown to be without action on the chloro-*tert.*-butyloxy acid under the conditions employed. The substance melting at 60–70° was dissolved in dil. aqueous sodium carbonate and to this solution there was added potassium permanganate solution until its color persisted for a few minutes, a large excess being avoided. After filtering off the manganese dioxide thus precipitated, the filtrate was immediately extracted with ether to remove benzaldehyde. Acidification of the sodium carbonate solution gave an oil which readily crystallized. Another crystallization from benzene gave pure α -chloro- β -*tert.*-butyloxyphenylpropionic acid; yield, 6 g., or 14%. The remainder of the material was an oil containing some crystals. The colorless crystals of the chloro-*tert.*-butyloxy acid retain benzene and, on standing, the melting point (83–85°) slowly rises because of the loss of benzene. Before analysis the finely powdered substance was allowed to stand in a vacuum desiccator over phosphorus pentoxide for about a week, when its melting point became constant at 94–94.5°. The benzene may also be removed by crystallization from chloroform.

Anal. Calcd. for $C_{13}H_{17}O_2Cl$: C, 60.80; H, 6.67; Cl, 13.81. Found: C, 60.81; H, 6.68; Cl, 14.15.

Structure of the Chloro-*tert*.-Butyloxy Acid.—To a solution of 5.4 g. of potassium hydroxide in 28 cc. of absolute ethyl alcohol there was added 3.8 g. of the chloro-*tert*.-butyloxy acid melting at 92–94°. After boiling under a reflux condenser for five hours, the alcohol was distilled, the residue dissolved in water and acidified. The oil thus precipitated was extracted with ether; after drying the ether solution and distilling the solvent, 3 g. of red, mobile oil was obtained. Efforts to separate a pure compound from the oil were without success. That it contained an unsaturated compound was indicated by the fact that it decolorized a solution of bromine in carbon tetrachloride, and its sodium carbonate solution rapidly reduced potassium permanganate. The oil was mixed with 100 cc. of 10% sulfuric acid solution and steam distilled until oil ceased to pass over. Extraction of the distillate with ether and distillation of the solvent, after drying, gave 0.9 g. of oil resembling acetophenone in appearance and odor. By treating it with semicarbazide hydrochloride and sodium acetate, acetophenone semicarbazone was obtained; m. p., 195–196°. A mixture of this substance with known acetophenone semicarbazone melted at the same temperature. The identity of the oil was further established by its reaction with hydroxylamine hydrochloride to give acetophenone oxime; m. p., 58–59°.

The aqueous solution remaining in the distilling flask after the steam distillation described above was extracted with ether. From this there was obtained 1.5 g. of reddish oil, which partially crystallized on adding a small amount of water and cooling in ice; wt., 0.3 g.; m. p., 82–84°. After this had been recrystallized from benzene several times and allowed to stand in a vacuum desiccator over phosphorus pentoxide, it melted at 104–105°, which corresponds with the melting point of anhydrous α -chloro- β -hydroxyphenylpropionic acid given by Glaser.¹²

Anal. Calcd. for $C_9H_9O_3Cl$: C, 53.86; H, 4.52; Cl, 17.67. Found: C, 53.89; H, 4.70; Cl, 17.31.

The formation of acetophenone and α -chloro- β -hydroxyphenylpropionic acid by these reactions shows that the alkoxyl group is in the beta position to the carboxyl group, and the substance is α -chloro- β -*tert*.-butyloxyphenylpropionic acid.

Reaction of Benzalacetophenone with Chlorine and *tert*.-Butyl Alcohol.—A solution of 15 g. of benzalacetophenone in 150 cc. of *tert*.-butyl alcohol was treated with 4.5 l. of chlorine in the manner described for cinnamic acid. Distillation of the *tert*.-butyl alcohol gave a colorless oil, which partially crystallized upon standing for several days. After filtering and allowing the filtrate to stand for about four weeks, another crop of crystals was obtained. From the first fraction there was obtained by recrystallization from alcohol 3.5 g. of α,β -dichloro- β -phenylpropiophenone melting at 113–114°. A mixture with the known dichloride of benzalacetophenone melted at the same temperature. The second fraction of crystals obtained as described above weighed 2 g. and melted at 80–90°. A fractional crystallization from alcohol yielded colorless crystals melting at 82–83°. This was found to be a stereo-isomer of α,β -dichloro- β -phenylpropiophenone, which has not hitherto been described.

Anal. Calcd. for $C_{18}H_{15}OCl_2$: C, 64.52; H, 4.33; Cl, 25.41. Found: C, 64.26; H, 3.99; Cl, 25.32.

That the substance is a stereo-isomer of benzalacetophenone dichloride, and not a structural isomer, was shown by its reaction with hydroxylamine to give diphenylisoxazole, which Goldschmidt⁸ showed to be the product of the same reaction with α,β -dichloro- β -phenylpropiophenone melting at 113°. To a solution of 0.35 g. of the low-melting dichloride (82–83°) in 13 cc. of 80% aqueous ethyl alcohol, there was added 0.18 g. of hydroxylamine hydrochloride. After bringing into solution by warming, dil. sodium hydroxide solution was added until tests with litmus showed an excess,

¹² Glaser, *Ann.*, 147, 82 (1868).

Crystals of diphenylisoxazole soon began to separate. After standing for 30 minutes, the solution was filtered and the filtrate was immediately poured into water, which precipitated the diphenylisoxazole; yield, 0.2 g. By recrystallization from alcohol, colorless flakes of the pure substance were obtained; m. p., 140.5–141°. No depression of the melting point was produced on mixing with known diphenylisoxazole (m. p. 140.5–141°), which was prepared by the reaction of hydroxylamine with the dichloride of benzalacetophenone melting at 113–114°.

The principal portion of the material resulting from the reaction of benzalacetophenone with chlorine and *tert.*-butyl alcohol was an oil which did not crystallize after standing for several months and which could not be obtained in the solid state by the use of solvents. In the hope of isolating the *tert.*-butyl hypochlorite addition product, the oil was subjected to a distillation at 5 mm. pressure. This, however, produced deep-seated decomposition, large quantities of gas being evolved. From the fraction boiling at 125–150° ω -chloro-acetophenone was separated; the other products were not identified, although the presence of benzoyl chloride was evident. The ω -chloro-acetophenone, after recrystallization from alcohol, melted at 55–55.5° and possessed the lachrymatory properties characteristic of this substance. Inasmuch as the melting point given in the literature is 58–59°, the crystals melting at 55–55.5° were further identified.

Anal. Calcd. for C_8H_7OCl : C, 62.12; H, 4.57; Cl, 22.93. Found: C, 61.68; H, 4.60; Cl, 23.24.

When treated with hydroxylamine hydrochloride according to the procedure of Korten and Scholl,¹³ it gave synphenylchloromethylketoxime (m. p., 88–89°), a reaction characteristic of ω -chloro-acetophenone.

Summary

1. The reaction of chlorine with a solution of cinnamic acid in absolute ethyl alcohol results in a low yield of α -chloro- β -ethoxyphenylpropionic acid. Oxidation of the hydrochloric acid formed in the reaction by means of potassium chlorate was shown to reduce greatly the amount of chlorine required, although the yield of the chloro-ethoxy acid was not materially improved. A solution of ethyl hypochlorite in carbon tetrachloride was found to be without action on cinnamic acid.

2. The reaction of chlorine with a solution of cinnamic acid in *tert.*-butyl alcohol results in the formation of α -chloro- β -*tert.*-butoxy-phenylpropionic acid.

3. The addition of *tert.*-butyl hypochlorite to benzalacetophenone, by its reaction with chlorine and *tert.*-butyl alcohol, could not be established. However, a new stereo-isomer of α,β -dichloro- β -phenylpropiophenone was isolated.

CLEVELAND, OHIO

¹³ Korten and Scholl, *Ber.*, **34**, 1901 (1901).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYL

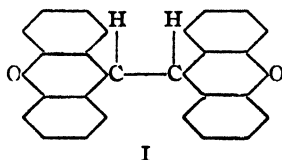
IV. DIXANTHYL AND DIXANTHYL-9,9'-DICARBOXYLIC ACID

BY JAMES B. CONANT AND BENJAMIN S. GARVEY, JR.

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It has been shown¹ that the aryl and *sec.*-alkyl derivatives of dixanthyl are dissociated in solution at room temperature and that the primary alkyl derivatives dissociate on warming their solutions. The parent substance dixanthyl (I) differs from these derivatives in that no color develops even on boiling its solution in methyl benzoate, and at room temperature it does not combine with oxygen. There is no reason, therefore, to believe that it dissociates into a free radical even at a com-



paratively high temperature.² The carbon-carbon linkage in this compound, however, is very reactive towards certain reagents which bring about cleavage of the molecule.

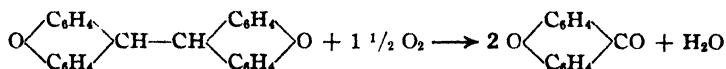
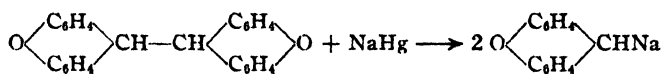
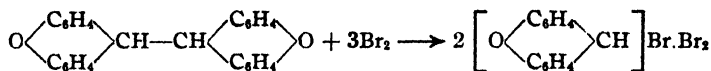
In dilute carbon disulfide solution bromine reacts with dixanthyl forming two molecules of the perbromide of xanthyl bromide. At room temperature, dixanthyl slowly dissolves in concd. sulfuric acid, yielding a brown solution; on hydrolysis xanthanol is obtained. By analogy with the reaction of acids on dissociated ethanes one would expect xanthane as the other product in this reaction but we were unable to prove its presence in the reaction mixture. The red sodium xanthyl is rapidly formed by shaking an ether solution of dixanthyl with either sodium-potassium alloy or 40% sodium amalgam (a liquid). Tetraphenylethane is similarly cleaved by sodium-potassium alloy³ but not by 40% amalgam. A 2% solution of dixanthyl in dibromobenzene begins to absorb oxygen at an appreciable rate at 150° and at 180–190° the oxidation is complete in five to six hours; the amount of oxygen absorbed corresponds to the for-

¹ Conant and Sloan, *THIS JOURNAL*, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925). Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

² Conant and Sloan [*THIS JOURNAL*, **45**, 2468 (1923)] prepared dixanthyl by reduction of the xanthanol in strong acid solution with vanadous chloride. They believed that the colored precipitate which is first formed might contain the free xanthyl radical in the solid state. We have reinvestigated this point and have failed to obtain any evidence that the pink precipitate contains "free xanthyl." The color seems to be due to small amounts of some highly colored impurity.

³ Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923).

mation of two molecules of xanthone. The pure compound at 225° absorbs the calculated quantity of oxygen in four to five hours, and xanthone can be isolated from the oxidation product.



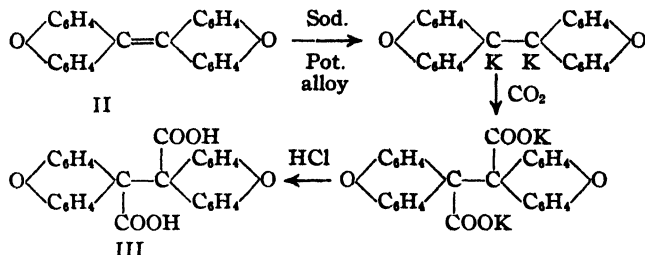
All these reactions are characteristic of dissociable ethanes, and when they take place with such a substance as hexaphenylethane, are usually interpreted as reactions of the free radical (for example, triphenylmethyl). With dixanthyl the reactions are slower and either require somewhat more drastic reagents (for example, 40% amalgam instead of 1% amalgam) or a higher temperature, as in the case of the absorption of oxygen. It seems to us highly improbable that these cleavage reactions of dixanthyl proceed through a free radical stage. We seem rather to be dealing with definite reactions of the *single* bond. Even in the case of the oxygen absorption of the colorless solutions of certain dialkyl dixanthyls the reaction may involve a very reactive carbon-to-carbon linkage and not a free radical. In the dixanthyl series we have at our disposal a series of compounds with considerable variations in the reactivity of the single linkage; at the top of the series are those substances like diphenyl-dixanthyl and di-*isopropyl*dixanthyl which dissociate in solution at 25°; at the bottom is the hydrogen compound dixanthyl itself.

It is worth noting that the cleavage of a single bond by halogens, acids, alkali metals and oxygen is strikingly parallel to the action of the same reagents on ethylenic derivatives. The only difference is that in the case of the unsaturated compounds the molecule as a whole stays intact as only one of the two linkages is cleaved. It is very probable, therefore, that the final explanation of the variations in the reactivity of the single bond and the double bond will be found to be closely allied if not identical.

Dixanthyl-9,9'-dicarboxylic Acid and its Ester

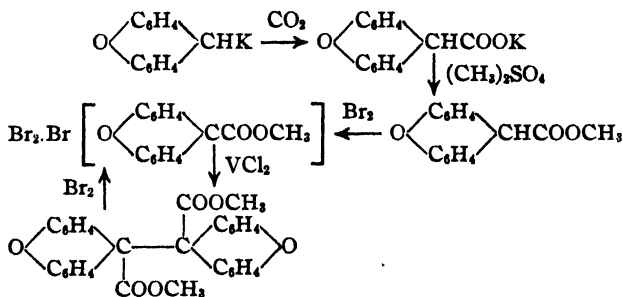
In order to compare the dissociating influence of a so-called negative group with that of aryl and alkyl groups, we have synthesized dixanthyl-9,9'-dicarboxylic acid (III) and its dimethyl ester by two methods. Dixanthylene (II) adds two atoms of alkali metal when shaken with sodium-potassium alloy. The resulting compound, on treatment with carbon dioxide, yields the salt of the dibasic acid. The reactions are outlined below; we have written the metallic compound as the potassium com-

pound but have no evidence as to whether sodium or potassium (or perhaps both) is actually involved in the reaction.



The acid may also be obtained by the reduction of 9-bromo-xanthanoic acid with vanadous chloride. The crystalline perbromide was actually employed; it is probably a xanthylum salt and analogous to the salts of the substituted xanthanols, which we have reduced to dixanthyls in an earlier work in this Laboratory. The bromoxanthanoic acid was obtained by bromination of the xanthanoic acid formed by the action of carbon dioxide on potassium xanthyl. This in turn can be prepared by the cleavage of dixanthyl with sodium-potassium alloy or by the action of the same reagent on xanthane. The dimethyl ester of dixanthyl-9,9'-dicarboxylic acid can be prepared by a similar bromination of the methyl ester of xanthanoic acid and subsequent reduction. It may also be prepared by the methylation of the sodium salt of the dibasic acid with dimethyl sulfate.

Dimethyl dixanthyl-9,9'-dicarboxylate reacts rapidly with bromine in carbon disulfide and forms the perbromide of the bromo-xanthanoic ester. It is thus possible to go back and forth from this compound to the dixanthyl di-ester by using either aqueous vanadous chloride or bromine in carbon disulfide.



A solution of dixanthyl-9,9'-dicarboxylic acid in ethyl benzoate in nitrogen becomes red on heating and the color disappears on cooling; this may be repeated a number of times. The first color becomes apparent at about 105°; at 140° a two per cent. solution is light cherry-red. The color darkens on further raising the temperature but above 185° an

irreversible decomposition takes place and the red color disappears. This decomposition is probably some sort of internal oxidation-reduction similar to that observed with the di-alkyl dixanthyls. Xanthanoic acid was isolated from a naphthalene solution of the dibasic acid which had been heated until the red color had appeared and then faded. A solution of the dimethyl ester showed the same reversible color changes on heating but unlike the acid the color showed no signs of fading after ten minutes at 200°; on cooling, the solution became colorless. The first color was visible at 115–120°, and above 175° the solution was cherry-red.

The red color of a solution of the ester or acid in boiling xylene was discharged by the addition of phenylhydrazine. Unfortunately, no crystalline products could be isolated from the reaction mixture. The color also disappeared when oxygen was bubbled through the hot solution. A small quantity of crystalline material was isolated from such an oxidized solution of the ester; analysis showed it to have the composition of the peroxide. The rates of oxygen absorption of the acid and ester were measured in the usual way, using bromobenzene as a solvent at room temperature, and *p*-dibromobenzene at higher temperatures. A solution of the ester at 25° absorbed no appreciable quantity of oxygen in 52 hours but the acid under the same conditions absorbed 9.3% of one mole. At higher temperatures the action is more rapid; carbon dioxide is evolved in the case of the acid and this was absorbed in sodium hydroxide before measuring the change in volume. At 120–130° a dilute solution of the acid reacted with 80% of one mole in six and a half hours. At 150–160°, a similar solution of the ester absorbed 54% in seven hours. A solution of the acid in sodium hydroxide was heated to boiling and oxygen bubbled through for three hours; xanthone was precipitated (about 20%) and on acidification considerable unchanged acid was obtained.

A comparison of the facts stated in the preceding paragraph with the behavior of other dixanthyl derivatives is of interest. The temperature at which dissociation first becomes appreciable, as judged by the appearance of color, is about the same for the ester and acid (115° for the ester, 105° for acid). It is considerably lower than the temperature required for appreciable dissociation of dimethyl-dixanthyl (about 160°) or dibutyl-dixanthyl (about 140°), but greater than that for dibenzyl-dixanthyl (about 80°). On the other hand, towards oxygen the compounds are much less reactive than the least reactive of the dialkyl dixanthyls, all of which in dilute solution absorb one mole of oxygen in less than a day, at 25°.

This marked unreactivity of the compounds towards oxygen is in accord with the only other work that has been done on the effect of negative groups on the dissociation of ethanes. Löwenbein⁴ has prepared the

⁴ Löwenbein, *Ber.*, **58**, 601 (1925).

bislactone of 2,2'-dioxytetraphenyl-succinic acid and has shown by colorimetric measurements that it is considerably dissociated in boiling toluene. The same author later showed that tetra-*p*-anisyl-succinonitrile begins to dissociate at 60–80° and tetraphenyl-succinonitrile at about 140°. The color of Löwenbein's free radicals was discharged by phenylhydrazine but only very slowly by oxygen; a 20% solution of the bislactone in boiling xylene was decolorized by a stream of oxygen in an hour. This rate is of the same order of magnitude as the rates of oxygen absorption by the dixanthyl dibasic acid, but very different, indeed, from those observed with all other dissociable ethanes. Löwenbein has explained this unreactivity of his radicals in terms of a splitting of the free valence between the ethane carbon atom and the oxygen atom of the carbonyl group.

Experimental Part

Reactions of Dixanthyl. (a) *Bromine*.—Five cc. of a 6% solution of bromine in carbon disulfide was added to a solution of 0.2 g. of dixanthyl in 10 cc. of the same solvent. An orange precipitate was formed; after it had been filtered off and washed with petroleum ether it melted with decomposition at 151–153°. A sample of the perbromide of xanthyl bromide was prepared by the action of gaseous bromine and hydrobromic acid on a carbon disulfide solution of xanthanol;⁵ it was identical with the bromide prepared from dixanthyl as shown by color, reactions and mixed melting point.

Anal. For perbromide bromine: Calcd.: 38.0. Found: 38.2.

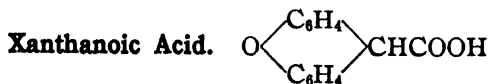
(b) *Sulfuric Acid*.—A tenth of a gram of dixanthyl was suspended in 30 cc. of concd. sulfuric acid. After 48 hours a brown solution was formed; this was filtered through asbestos, poured onto ice and neutralized. The white precipitate was taken up in ether which was then evaporated. On treating the residue with perchloric acid in dry ether, a yellow precipitate of xanthanol perchlorate (m. p. 218–219°) was obtained. It was identified by a mixed-melting-point determination.

(c) *Cleavage by Alkali Metals*.—A solution of 0.18 g. of dixanthyl in 10 cc. of absolute ether was shaken with 1 cc. of a liquid sodium-potassium alloy (10 parts of potassium and 4 parts of sodium) in dry nitrogen. The solution became red in about a minute and after two and a half hours there was a considerable red precipitate. After treating with carbon dioxide, decomposing the excess of alloy with alcohol and acidifying, 0.12 g. of xanthanoic acid, m. p. 215–217° (see below), was obtained. In a similar experiment with 40% sodium amalgam (a liquid) the solution acquired the characteristic red color of sodium xanthyl, but on working up the product after two and a half hours, only a very small amount of xanthanoic acid was obtained. One per cent. sodium amalgam gave no color even on prolonged shaking.

(d) *Oxygen Absorption*.—A tenth of a gram of dixanthyl dissolved in 9 g. of molten *p*-dibromobenzene absorbed 9.2 cc. of oxygen (N. T. P.) in 6.5 hours; at 148–155° in two other experiments, 2.7 and 2.1 cc. were absorbed in 5.75 and 6.75 hours, respectively. A blank showed that the dibromobenzene itself absorbed no oxygen under similar conditions. To oxidize 0.1 g. of dixanthyl to xanthone requires 9.3 cc. of oxygen (N. T. P.). A tenth of a gram of dixanthyl without any solvent absorbed the calculated quantity of oxygen in from 3 to 4.5 hours; xanthone was isolated and identified by mixed-melting-point determination. The apparatus used in measuring the rate of oxygen

⁵ Gomberg and Cone, *Ann.*, **376**, 193 (1910).

absorption at elevated temperatures consisted of a bulb of about 20 cc. capacity heated in a paraffin bath and connected to a gas buret having mercury as the containing liquid.

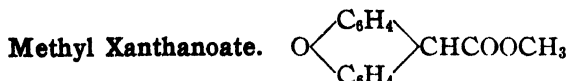


(a) **Preparation from Dixanthyl.**—In a typical run for the preparation of this acid, 2.25 g. of dixanthyl in 150 cc. of dry ether was shaken overnight with 10 cc. of sodium-potassium alloy under nitrogen in a 500 cc. glass-stoppered distilling flask with the side arm sealed off. The solution was then brick red and there was a brick-red precipitate. The flask was then cooled in a bath of ice and salt and dry carbon dioxide was passed in by breaking off the tip of the side arm. Common ether was then added and the contents of the flask were washed into a beaker. The moisture in the ether caused the alloy to coagulate so that it could easily be removed by a small glass dipper. Water was then added to dissolve the sodium salt, and the ether and water layers were separated. The alkaline water layer was acidified. This threw out a copious, very finely divided precipitate which was extracted with ether. The ether was dried over calcium chloride and evaporated. The residue was recrystallized from 50% ethyl alcohol. The product crystallized in long, white needles which softened slightly at 222° and melted at 223–224°. The yield of recrystallized product was 1.6 g.

(b) **Preparation of Xanthanoic Acid from Xanthane.**—In the preparation of the acid 0.3 g. of xanthane in 15 cc. of dry ether was shaken for ten minutes with 5 cc. of sodium-potassium alloy. The solution was brick red and there was some brick-red precipitate. This sodium xanthyl was treated with carbon dioxide, as in the previous case. A small amount of acid was obtained which was recrystallized from 50% ethyl alcohol and then from ether and petroleum ether; m. p., 218–219°. When mixed with some of the acid obtained from dixanthyl (m. p. 222–223°) the mixed melting point was 221–222°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_5$: C, 74.3; H, 4.4. Found: C, 74.7; H, 4.6. Equiv. wt. by titration in 50% alcohol with standard sodium hydroxide solution (phenolphthalein indicator). Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_5$: 226. Found: 220, 226.

On heating to 290–300°, xanthanoic acid decomposes, giving carbon dioxide and xanthane. Bromination in carbon disulfide produced a dark red precipitate (m. p., 162–163°) and evolution of hydrobromic acid. The red precipitate on reduction with vanadous chloride in concd. hydrochloric acid yielded dixanthyl-9,9'-dicarboxylic acid (see below).



Xanthanoic acid may be converted into its methyl ester by methylation of the sodium salt with dimethyl sulfate at 100° or by the action of thionyl chloride and absolute methyl alcohol. The ester can be recrystallized from methyl alcohol; it melts at 85–86°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_5$: C, 75.0; H, 5.0. Found: C, 75.1; H, 5.0.

Mol. wt. in freezing benzene. Subs., 0.1354 g.; 0.2522 g.; solvent, 17.37 g.; Δt , 0.172, 0.320; $K = 5.12$. *Mol. wt.* Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_5$: 240 Found: 232, 233.

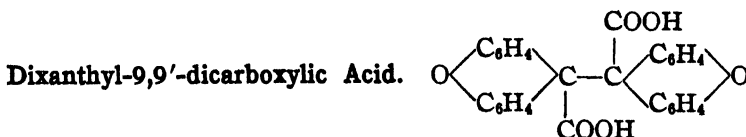
Perbromide of Methyl-9-Bromo-xanthanoate.



Bromination of the methyl ester in carbon disulfide yielded a red precipitate with

evolution of hydrogen bromide. It was purified by washing with petroleum ether; it melted at 158–159° with decomposition.

Anal. for perbromide bromine. Calcd. for $C_{18}H_{18}O_4Br$: Br, 33.4. Found: 33.5.



Preparation from Dixanthylene.—In a typical run 2.4 g. of dixanthylene, 350 cc. of dry ether and 15 cc. of sodium-potassium alloy under dry nitrogen, were shaken for 12 hours in a glass-stoppered distilling flask with the side arm sealed off. The solution was a deep reddish-purple and there was a dark precipitate. The flask was cooled in an ice-and-salt bath and carbon dioxide was introduced by breaking the tip off the side arm. Considerable white precipitate formed. The contents of the flask were washed into a beaker with common ether. The moisture caused the alloy to coagulate and it was removed with a small, glass dipper. Water was added and the mixture shaken. The two layers were then separated. The ether was sucked out of the water layer, which was turbid. The water layer was filtered four times before a clear, yellow solution was obtained. When this solution was then acidified considerable precipitate formed which quickly coagulated and was filtered off, washed well and dried. It commenced to darken at 125° and decomposed up to 155°.

Numerous attempts to purify the acid by crystallization from various solvents failed; the only way to purify the material was to dissolve in aqueous alkali, filter and reprecipitate with acid. When the acid which had been precipitated from a clear alkaline solution was redissolved after standing, there was usually a small residue of xanthone. The clear alkaline solutions slowly deposited small amounts of the same material, evidently due to oxidation by the air.

Anal. Calcd. for $C_{28}H_{18}O_6$: C, 74.7; H, 4.0. Found: C, 74.5; H, 4.3.

Equiv. wt. by titration (phenolphthalein indicator). Calcd. for $\frac{1}{2} C_{28}H_{18}O_6$: 225. Found: 221, 230.

Oxidation with Oxygen.—Half a gram of the acid was dissolved in 15 cc. of 5% sodium hydroxide, the solution diluted to 30 cc. and heated to boiling for three hours under a return condenser while a current of oxygen was bubbled through. After cooling and standing overnight, 0.075 g. of xanthone was filtered off. On acidification considerable dixanthyl-9,9'-dicarboxylic acid was obtained, somewhat pink in color. It melted, with decomposition, at 110–150° and was further identified by analysis. (Found: C, 74.0; H, 4.3.)

When the acid was dissolved in *p*-dibromobenzene and heated in oxygen at 150–160° there was no change in volume after seven hours. However, when the apparatus was disconnected and the bulb submerged in concd. potassium hydroxide, 6 cc. was drawn into the bulb, showing that carbon dioxide was formed. For further experimentation a tube filled with slightly moist potassium hydroxide was inserted between the reaction bulb and the gasometer. With this apparatus a solution of 0.15 g. of the acid in 7 g. of dibromobenzene absorbed oxygen as follows: at 120–130°, 80% of one mole in 6.5 hours and 100% in 13 hours.

The rate of oxidation by oxygen in bromobenzene at 25° was determined in the usual manner. Only 9.3% of one mole was absorbed in three days.

Color on Heating.—A solution of 0.225 g. of the acid in 10 cc. of ethyl benzoate was heated in an atmosphere of nitrogen. The temperature was fixed by plunging the tube in a hot paraffin bath. At 90° there was no color; at 105° the first color became

apparent, which faded on cooling. This was repeated. At 150° the color became a light cherry-red; this faded on cooling, but the solution remained somewhat more colored than it was originally. At 180–200° the red color faded to yellow in about five minutes.

A sample of 0.2 g. of the acid was mixed with 10 g. of naphthalene and heated in a paraffin bath under nitrogen until the color faded. When cold, the tube was broken. The contents were dissolved in ether and this solution was extracted with sodium carbonate. Both the ether and the alkaline layers were yellow. The precipitate formed by the acidification of the alkali layer did not coagulate and was, therefore, extracted with ether, which was dried and evaporated. A yellow oil and a few crystals were obtained. This product was taken up in hot 50% ethyl alcohol and the solution filtered from a few crystals which melted above 240° and were not identified. When cold, the solution was filtered but no product was obtained. It was then extracted with ether which was dried and evaporated. Gummy crystals were obtained. They were washed in 50% ethyl alcohol. In this way a small quantity of crystals of xanthanoic acid was obtained (m. p. 218–220°) and identified by a mixed-melting-point determination.

When a solution of the acid in xylene was heated almost to boiling, the reddish color of the radical was quite apparent. When a solution of phenylhydrazine in xylene was added to this hot solution the radical color faded at once. No precipitate was formed. Several attempts to isolate xanthanoic acid from this reaction mixture failed, the only product being a yellow oil.



The dibasic acid was converted to its dimethyl ester by boiling a solution of it in 5% sodium hydroxide with dimethyl sulfate, the gummy precipitate being filtered from the still strongly alkaline solution. It was also prepared by the reduction of the perbromide of bromo-xanthanoic ester as follows. A solution of 0.5 g. of the perbromide in 125 cc. of concd. hydrochloric acid was treated with 3 cc. of 0.5 *N* vanadous chloride. A pinkish precipitate was formed. It was dissolved in ether, the solution extracted with aqueous sodium hydroxide, the ether solution then dried and the ether evaporated. A flaky, amorphous solid was left, melting over the range 90–110°. The ester could not be crystallized from any solvent that was found. On evaporating a dry ether solution it was obtained as an amorphous, flaky solid; an alcoholic solution evaporated in a vacuum left a yellow gum which hardened to a pliable solid. A similar solid could be obtained by precipitation with water from methyl alcohol. All samples melted indefinitely between 85 and 110°, but could be dried in a vacuum for analysis and molecular-weight determination.

Anal. Calcd. for $C_{30}H_{22}O_8$: C, 75.3; H, 4.6. Found: C, 75.2; H, 4.9.

Mol. wt. in freezing benzene. Subs., 0.2708 g., 0.5876 g. Solvent, 17.37 g.; Δt , = 0.208°, 0.419°. *Mol. wt.* Calcd.: 478. Found: 393, 414.

A solution of the ester in ethyl benzoate (0.24 g. in 10 cc.) heated in nitrogen showed a faint color at 115°; at 125° the color was deeper and faded on cooling. This could be repeated many times. Above 125° the color deepened, being cherry-red at 170°. It did not fade on keeping at 200° for ten minutes, but faded on cooling; on again heating to 200° the cherry-red color deepened as before. These experiments were performed both with the material prepared by esterification of the dibasic acid and by reduction of the perbromide; the reversible appearance of color was the same with both samples,

A solution of the ester in carbon disulfide (0.14 g. in 8 cc.) when treated with bromine gave a red precipitate *without* evolution of hydrogen bromide. This precipitate was shown to be the perbromide of methyl bromo-xanthanoate by mixed melting point (158–159°) and by analysis.

Oxygen Absorption.—When 0.14 g. of the dimethyl ester was dissolved in 10 cc. of bromobenzene in the usual oxygen-absorption apparatus, there was no absorption in 52 hours.

The oxygen absorption at high temperatures was determined in the same apparatus which was used for the acid, using 0.14 g. of the ester and 7 g. of *p*-dibromobenzene. The absorption at 120–130° was 36.4% of one mole in seven hours. At 150–160° it was 53.4% of one mole in seven hours and 87.7% of one mole in 11 hours.

Two samples of 0.1 g. of the dimethyl ester were dissolved in 5 cc. of xylene in test-tubes under nitrogen and the solutions heated to boiling. The color deepened to a decided red tint. A stream of nitrogen was passed into the first, just above the surface of the liquid. The color remained in this solution for 35 minutes and then faded on cooling. Fifteen minutes later the color again deepened when the solution was heated, and faded on cooling. Ten minutes later this was again repeated. A stream of oxygen was bubbled through the second tube while the xylene was boiling. The red color faded in about five minutes and there was no further change on subsequent heating and cooling. The xylene was steam distilled from the second solution, leaving a yellow oil. Attempts to crystallize this oil from methyl alcohol yielded a small quantity of white crystals, m. p. 176°, with gas evolution. Further small quantities of this product were obtained in subsequent, similar runs.

Anal. Subs., 0.01137: CO₂, 0.02922; H₂O, 0.00426. Calcd. for C₂₀H₂₂O₄: C, 70.6; H, 4.3. Found: C, 70.1; H, 4.2.

A red solution of the ester in boiling xylene was treated with phenylhydrazine in nitrogen. After seven minutes at the boiling point, the color had faded and no more color was developed on subsequent heating and cooling. No crystalline products could be isolated from the reaction mixture.

Summary

1. The following cleavage reactions of dixanthyl have been demonstrated: (a) with bromine in dilute carbon disulfide; (b) with sodium-potassium alloy and 40% sodium amalgam; (c) with concd. sulfuric acid; (d) oxidation by oxygen above 150°. There is a striking parallel between these reactions of the single carbon bond and addition reactions of ethylenic compounds.

2. Dixanthyl-9,9'-dicarboxylic acid and its dimethyl ester have been synthesized by two methods. Solutions of these compounds, when heated above 100°, show reversible color changes characteristic of dissociable ethanes. Judged by the temperature required for appearance of radical color, the carboxy and carbomethoxyl groups have a slightly greater dissociating influence than primary alkyl groups. In spite of this, the compounds are only very slowly oxidized by oxygen even above 100°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY,
No. 302]

THE MECHANISM OF THE WURTZ-FITTIG REACTION¹

By W. E. BACHMANN AND H. T. CLARKE

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In a search for a convenient laboratory method for the preparation of relatively large quantities of biphenyl, one of us with T. F. Murray, some three years ago, investigated the action of sodium on chlorobenzene at the boiling temperature. It was found that while biphenyl was produced in about 20% of the calculated yield, it was accompanied not only by a high proportion of benzene, but the residue, on distillation with steam, yielded a hydrocarbon of higher boiling point, which melted at 57° and was apparently identical with the hydrocarbon melting at 57–58° isolated by Weiler² from the products of the action of sodium upon bromobenzene. Analysis and molecular-weight determination of this compound show it to be a diphenylbenzene; since the *meta* and *para* isomers are well known, the new compound must be the *ortho* derivative. This has been confirmed by synthesis.

We have also been able to isolate two other hydrocarbons of high molecular weight, which are not volatile with steam; these are triphenylene, which was isolated (although not identified) by Schultz³ from the products of the action of sodium upon bromobenzene according to the directions of Fittig,⁴ and a hydrocarbon, C₂₄H₁₈, which we have proved by synthesis to be *o,o'*-diphenylbiphenyl. All three of these hydrocarbons were isolated by Weiler who, however, made no attempt to characterize them beyond determining their molecular weight.

Two other products, melting at 167–168° and 151–152°, respectively, were described by Weiler, but we have been unable to detect either of them among the products of the action of sodium upon chlorobenzene. On the other hand, like Weiler, we have isolated very small amounts of *p*-diphenylbenzene from among the products of our reaction.

A considerable quantity of a sirupy hydrocarbon is also formed; analysis shows it to consist of hydrocarbons of approximately the same empirical composition and molecular weight as the above products, but we have no clue as to their constitution.

The mechanism of the Wurtz-Fittig reaction has received ample discussion, particularly in the recent papers of Schlubach and Goes⁵ and Goldschmidt and Schön.⁶ The alternative theories advanced in

¹ Reported before the Organic Division, American Chemical Society, at Richmond, Virginia, April, 1927.

² Weiler, *Ber.*, 29, 115 (1896).

³ Schultz, *Ann.*, 174, 228 (1874). Dreher and Otto, *Ann.*, 154, 99, footnote (1870). Carstanjen, *J. prakt. Chem.*, [1] 110, 80 (1870).

⁴ Fittig, *Ann.*, 132, 202 (1864).

⁵ Schlubach and Goes, *Ber.*, 55, 2889 (1922).

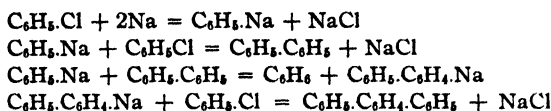
⁶ Goldschmidt and Schön, *Ber.*, 59, 948 (1926).

these papers, involving on the one hand the formation of free radicals, and on the other the reaction between sodium aryls⁷ and halogen compounds, are equally capable of interpreting the formation of benzene⁸ and biphenyl.

Now Schorigin⁹ has demonstrated that metallic alkyls can exchange their metal for hydrogen when treated with aromatic hydrocarbons, and we have been able to show that an analogous migration of sodium takes place in the sodium aryls.

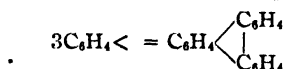
A suspension of mercury di-*p*-tolyl was converted into the corresponding sodium derivative by the action of metallic sodium in the presence of benzene; by the action of carbon dioxide there were formed not only *p*-toluic acid but also benzoic and phenylacetic acids, indicating the partial migration of sodium (either simultaneously with the replacement of the mercury or subsequently thereto) from the *para* carbon atom of the toluene to the side chain and to the benzene in which the mixture was suspended.

By assuming the transference of sodium from sodium phenyl to biphenyl, an explanation of the formation of diphenylbenzene is readily forthcoming.

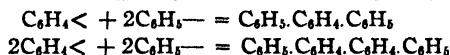


The diphenylbiphenyl may be regarded as being formed in an analogous manner from diphenylbenzene.

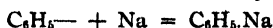
On the other hand, this type of mechanism cannot be made to account for the formation of triphenylene, and we regard the presence of this compound among the reaction products as decisive in favor of the free radical explanation. This involves the interaction of two free phenyl radicals to form benzene and free phenylene, $2 \text{C}_6\text{H}_5\cdot = \text{C}_6\text{H}_6 + \text{C}_6\text{H}_4\cdot$, which condenser either with itself, to form triphenylene



or with phenyl, to form diphenylbenzene and diphenylbiphenyl.



We are, however, far from suggesting that sodium aryls play no part in the Fittig reaction, for it has been shown by Schlenk¹⁰ that free aryls and alkali metals can unite to form metallic aryls.



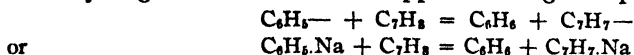
⁷ Krafft and Göttig, *Ber.*, **21**, 3180 (1888). Nef, *Ann.*, **308**, 291 (1899). Acree, *Am. Chem. J.*, **29**, 588 (1903). Hilpert and Grüttner, *Ber.*, **46**, 1679 (1913). Schlenk and Holtz, *Ber.*, **50**, 262 (1917).

⁸ Wieland, Popper and Seefried, *Ber.*, **55**, 1816 (1922).

⁹ Schorigin, *Ber.*, **43**, 1938 (1910).

¹⁰ Schlenk, *Ber.*, **49**, 608 (1916).

In the hope of throwing more light on the problem, the reaction between sodium and chlorobenzene was carried out in the presence of an excess of toluene, with the idea that this latter hydrocarbon might act as a hydrogen donor and thus appear among the products of reaction.

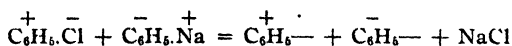


This was found to be the case; the formation of biphenyl was apparently entirely suppressed, and the fraction which should have contained it consisted of a mixture of *p*-methylbiphenyl and diphenylmethane. The yield of benzene rose to 34% in the case when the sodium was added to the mixture of chlorobenzene and toluene and to 46.5% when the chlorobenzene was added to the sodium suspended in the toluene.

This participation of the toluene in the reaction recalls the observation of Schorigin¹¹ on the action of sodium upon mixtures of mercury diethyl and benzene, toluene, etc., in the presence of carbon dioxide, whereby benzoic acid, phenylacetic acid, etc., are formed. It also finds an analogy in the experiment above quoted in which we have obtained benzoic and phenylacetic acids by treating mercury di-*p*-tolyl successively with sodium and carbon dioxide in the presence of benzene.

Similarly, when chlorobenzene is added to a suspension of sodium in hot dimethylaniline, the latter compound acts as a donor of hydrogen; 49% of the chlorobenzene is recovered as benzene, biphenyl is formed in only minute amounts, and the pitch-like residue contains nitrogen. This pitch, the nature of which was not closely investigated, is insoluble in dil. hydrochloric acid, and appears to contain compounds related to diphenylamine, since its solution in acetic acid readily develops a blue color on exposure to air. Basic compounds are also formed in small (about 2%) amounts; no systematic attempt was made to separate them but derivatives of benzyraniline appear to be present, as is indicated by the formation of benzaldehyde on oxidation in acid solution.

The fact that the yield of benzene appears never to exceed 50% of that theoretically obtainable from the chlorobenzene in the presence of a hydrogen donor, leads us to advance the tentative hypothesis that the free phenyl radical can exist in two electromeric forms, of which only one is capable of accepting hydrogen under the given conditions. The formation of these types of opposite polarity could be explained by postulating their formation by the interaction of chlorobenzene and sodium phenyl.



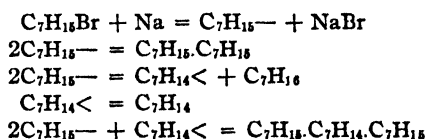
It is noteworthy that no *o*-diphenylbenzene could be detected in the residues from about 5 kg. of pyrogenic biphenyl, which yields relatively large quantities of *m*- and *p*-diphenylbenzene and a small amount of triphenylene.¹² The hypothesis that this last compound is formed by the dehydrogenation of any *o*-diphenylbenzene initially produced was disproved by passing the latter substance through a red-hot tube, in an atmosphere of carbon dioxide, when only biphenyl and a little carbon were found together with unchanged *o*-diphenylbenzene.

¹¹ Schorigin, *Ber.*, **41**, 2723 (1908); Ref. 9.

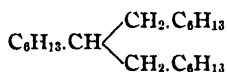
¹² Compare Schmidt and Schultz, *Ann.*, **203**, 135 (1880). Mannich, *Ber.*, **40**, 164 (1907).

The Wurtz synthesis of aliphatic hydrocarbons appears to proceed along analogous lines. When *n*-heptyl bromide is treated at the boiling temperature with sodium, the following products are formed: heptane, 9%; heptylene, 3%; tetradecane, 67%; heneicosane, 3%, as well as hydrocarbons of higher molecular weight. A qualitative experiment with *iso*-amyl bromide and sodium yielded a pentadecane analogous to the above heneicosane.

Michael,¹³ who noted the formation of alkylene and the paraffin corresponding to it, considered that hydriodic acid was first eliminated and that the nascent hydrogen, resulting from the action of sodium upon it, converted a part of the alkylene into paraffin. This explanation takes no account of the formation of products of high molecular weight, and we believe that the facts can be more satisfactorily explained by the assumption of free radicals.



The formation of alkylene¹⁴ is represented as being preceded by that of free alkylidene, part of which reacts with free alkyl to form the triple compound. The chain of reasoning in this instance is incomplete, owing to the difficulty in determining the constitution of the heneicosane, which should, according to the above hypothesis, possess the structure



Analogous reactions have been observed among the alkyl magnesium halides. Späth¹⁵ showed that when the alkyl group contains two or more carbon atoms, the action of alkyl halides on alkyl-magnesium halides consists not only in the direct union of the participating alkyl groups but also in the formation of alkylene and the corresponding paraffin, while Fuson,¹⁶ in a recent study of the action of benzyl chloride upon methyl-magnesium iodide, noted as the principal reaction the formation of equivalent quantities of dibenzyl and ethane, with the formation of ethylbenzene as a side reaction. Both of the above cases can be readily explained by assuming the intermediate formation of free radicals.

¹³ Michael, *Am. Chem. J.*, **25**, 429 (1901).

¹⁴ It is noteworthy that the action of sodium upon bromocyclopentane leads to very poor yields of dicyclopentyl and much cyclopentene [Zelinsky, Titz and Fatejew, *Ber.*, **59**, 2580 (1926)]. The formation of cyclopentane is not recorded.

¹⁵ Späth, *Monatsh.*, **34**, 1965 (1913).

¹⁶ Fuson, *THIS JOURNAL*, **48**, 2681 (1926).

Experimental Part

Action of Sodium on Chlorobenzene.—Five kg. (44.4 moles) of chlorobenzene was heated in a 12-liter Pyrex flask, provided with an efficient stirrer and a reflux condenser, the inner tube of which was constructed of brass tubing of 15–20 mm. internal diameter. When boiling began the flame was extinguished and 460 g. (20 g. atoms) of sodium was added, piece by piece, through the condenser, at such a rate that the mixture boiled as rapidly as possible without loss of vapor. Vigorous stirring was maintained throughout the addition, which required four to five hours. When all had been added, the rather pasty mixture was allowed to cool somewhat and subjected to steam distillation until all of the unchanged chlorobenzene had been driven over. The distillate was separated and the oil carefully fractionated through a bubbler column¹⁷ when the following fractions were obtained: up to 83°, 407 cc.; 83–95°, 14 cc.; 95–110°, 8 cc.; 110–125°, 26 cc.; 125–130°, 28 cc.; from which the total amount of benzene was estimated at 427 cc. or 375 g., corresponding to 4.8 moles or 24%. The balance of the chlorobenzene was distilled through the column, and the small amount of residue containing biphenyl was joined to the dark, tarry residue from the steam distillation.

This was separated from the solution of sodium chloride and distilled under 15 mm. pressure through a short fractionating column. The following fractions were collected: up to 126°, 14 g.; 126–130°, 330 g.; 130–150°, 20 g.; 150–175°, 25 g.; 175–190°, 14 g.; 190–200°, 176 g.; 220–225°, 33 g.; 225–250°, 62 g.; residue, 350 g. Fraction 126–130° (15 mm.) consisted of almost pure biphenyl. Chlorine could not be detected in any of the fractions distilling above 130° (15 mm.).

***o*-Diphenylbenzene.**—The fraction 190–200° (15 mm.), on cooling, solidified to a mass of long, heavy needles, the setting-point being 50–51°. On recrystallizing from methyl alcohol, large, colorless monoclinic prisms were obtained which melted at 57°; the mother liquor, on evaporation at ordinary temperature, yielded a further crop of the same crystals contaminated with a little oily impurity. Further recrystallization did not raise the melting point above 57°. The compound boils under atmospheric pressure at 332° (corr.). It is somewhat soluble in cold methyl alcohol, and extremely readily in acetone and in chloroform.

Anal. Calcd. for C₁₈H₁₄: C, 93.87; H, 6.13. Subs. 0.2079, 0.2317: CO₂, 0.7148, 0.7960; H₂O, 0.1154, 0.1275. Found: C, 93.80, 93.72; H, 6.21, 6.16.

Mol. Wt. Ebullioscopic method of Menzies and Wright;¹⁸ solvent, benzene. Solvent, 25.296. Subs., 0.2473, 0.5807, 0.9191; Δt , 0.1084°, 0.2546°, 0.4021°. Calcd.: 230. Found: 235, 235, 236.

By oxidation of 5 g. of *o*-diphenylbenzene with chromic acid in acetic acid, according to the method employed by Kuhn and Winterstein¹⁹ for the oxidation of *p*-diphenylbenzene, there was obtained 0.2 g. of an acid which after recrystallization from petroleum ether melted at 108–110° and showed no change in melting point on mixing with *o*-phenylbenzoic acid prepared from fluorenone. When heated with phosphorus pentachloride it yielded yellow crystals of fluorenone. The corrected melting points and boiling points of the isomeric diphenylbenzenes were determined under the same conditions.

Diphenylbenzene	M. p., °C.	B. p., °C.
<i>o</i>	57	332
<i>m</i>	87	365
<i>p</i>	213	376

¹⁷ Clarke and Rahrs, *Ind. Eng. Chem.*, **18**, 1092 (1926). A column having less than one-half the linear dimensions of that originally described was found to be entirely satisfactory.

¹⁸ Menzies and Wright, *This Journal*, **43**, 2314 (1921).

¹⁹ Kuhn and Winterstein, *Ber.*, **60**, 434 (1927).

***p*-Diphenylbenzene.**—The fraction boiling at 200–225° (15 mm.) partially solidified on long standing. The solids were separated by moistening the mass with acetone and filtering. On recrystallization from acetone there was obtained a small quantity of leaflets which on recrystallization from a mixture of chloroform and acetone melted at 210° (corr.) and were identical with *p*-diphenylbenzene obtained by the action of a hot wire on benzene. The total amount obtained was 0.15 g.

The mother liquor from the *p*-diphenylbenzene yielded about 3 g. of *o*-diphenylbenzene, but the greater part of this fraction consisted of an uncrystallizable sirup.

Triphenylene.—The fraction boiling at 225–250° (15 mm.), the bulk of which passed over at about 240°, was recrystallized from a mixture of chloroform and methyl alcohol, which removed some pale yellow, sirupy material. The product, which melted at 110–115° and was evidently a mixture, was twice recrystallized from chloroform, when colorless needles melting at 199° (corr.) were obtained. The melting point was not changed on recrystallization from acetone. The boiling point was found to be 425° (corr.).

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 24.546. Subs., 0.2498, 0.4898, 0.6475, 0.7871; Δt , 0.1169°, 0.2264°, 0.2965°, 0.3691°. Calcd. for $C_{18}H_{12}$: 228. Found: 227, 230, 232, 227.

On mixing a cold saturated solution in acetone with a saturated solution of picric acid in the same solvent, the picrate separated as a yellow crystalline precipitate. On recrystallization from acetone it formed long, yellow needles which melted at 223° (corr.). This picrate was identified with the triphenylene picrate obtained from the residues of biphenyl produced by the action of a red-hot wire on benzene.

***o,o'*-Diphenylbiphenyl.**—The chloroform mother liquor from the triphenylene was evaporated to dryness and the residue recrystallized from acetone. Two types of crystal were obtained, the long, fine needles of triphenylene and some more massive pyramids. After decanting the mother liquor, the mixture was gently stirred for a few seconds with cold acetone; the solubilities of the two compounds appeared to be about the same, but the fine needles dissolved more rapidly. By repeating this procedure three or four times, all the triphenylene was removed and the residual crystals were finally recrystallized from acetone. The product forms large tetragonal or rhombic pyramids which melt at 118° and boil at 420° (corr.). It is readily soluble in acetone and chloroform and almost insoluble in cold methyl alcohol. It appears to form no compound with picric acid.

Anal. Subs., 0.1980, 0.1957: CO_2 , 0.6845, 0.6767; H_2O , 0.1056, 0.1023. Calcd. for $C_{24}H_{18}$: C, 94.12, H, 5.88. Found: C, 94.31, 94.29; H, 5.95, 5.85.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 23.905. Subs., 0.2047, 0.4396, 0.5900, 0.7895; Δt , 0.0799°, 0.1619°, 0.2180°, 0.3455°. Calcd.: 306. Found: 298, 296, 295, 292.

The mother liquor from the triphenylene and diphenylbiphenyl on concentration yielded a pale yellow sirup, which was freed of solvent by warming under reduced pressure. It was readily soluble in acetone and chloroform, but only slightly in methyl alcohol; it was indistinguishable from the principal constituent of the fraction collected at 220–225° (15 mm.).

Anal. Subs., 0.2224: CO_2 , 0.7635; H_2O , 0.1173. Found: C, 93.70; H, 5.90.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 24.465. Subs., 0.3352, 0.5850, 0.9583; Δt , 0.1392°, 0.2417°, 0.3656°. Found: 257, 257, 265.

Synthesis of *o,o'*-Diphenylbiphenyl.—An intimate mixture of 4 g. of *o*-iodobiphenyl, prepared from fluorenone by the method of Graebe and Rateanu,²⁰ and 5 g. of copper

²⁰ Graebe and Rateanu, *Ann.*, 279, 257 (1894).

bronze (Naturkupfer C) was heated at 260° for 20 minutes. The product was cooled and extracted with acetone in a Soxhlet apparatus. The extract was boiled with charcoal, filtered and concentrated; large, colorless pyramids separated on cooling. The yield was 1.5 g. (72% of the calculated amount) of a product melting at 115–116°. On recrystallization from a mixture of alcohol and benzene it melted at 116–117°, and a mixture of it with the *o,o'*-diphenylbiphenyl obtained from chlorobenzene showed no change in melting point.

Synthesis of *o*-Diphenylbenzene.—A mixture of 5 g. of *o*-iodobiphenyl, 10 g. of *o*-iodobenzene and 15 g. of copper bronze (Naturkupfer C) was heated in a sealed tube at 240° for three hours. The product solidified on cooling. It was extracted with benzene in a Soxhlet apparatus and the extract boiled with charcoal, filtered and freed from solvent by distillation. The residue was distilled under 2 mm. pressure and the following fractions were collected: 110–130°, 2 g.; 160–170°, 2 g.; above 200°, 1 g. The fraction boiling at 110–130° (2 mm.) was recrystallized from alcohol and found to consist of biphenyl. The fraction boiling at 160–170° was dissolved in warm methyl alcohol; on cooling, large prisms were obtained which melted at 55° and boiled at 320–325° (uncorr.). A mixture of this material with the *o*-diphenylbenzene obtained from chlorobenzene melted at 55–56°; a sample became oily at room temperature on mixing with biphenyl. The fraction boiling above 200° was washed with methyl alcohol, and the undissolved crystals, amounting to 0.5 g., were found to be identical with the *o,o'*-diphenylbiphenyl obtained by heating copper bronze and *o*-iodobiphenyl alone.

Action of Sodium on Chlorobenzene in the Presence of Toluene.—A. To a mixture of 2500 g. (22.2 moles) of chlorobenzene and 4600 g. (50 moles) of toluene was added 460 g. of sodium, exactly as in the previous experiment. The mixture was steam distilled and the distillate separated and fractionated. The resulting benzene was estimated as 603 g. (7.74 moles). The residual tar, on long standing, partially crystallized but it was not further examined.

B. To a suspension of 460 g. (20 g.-atoms) of sodium in 4600 g. (50 moles) of boiling toluene was added, with stirring, 2500 g. (22.2 moles) of chlorobenzene at such a rate that the mixture boiled vigorously but without loss of vapor. This required about five hours. The products were worked up exactly as in the experiment in which chlorobenzene alone was employed. Estimation of the benzene in the steam distillate showed the presence of 725 g. (9.3 moles). Distillation of the high-boiling portions under 20 mm. pressure yielded the following fractions: up to 135°, 14 g. of oil; 135–150°, 120 g. of oil; 150–170°, 19 g. of oil; 170–200°, 7 g. of solid; 200–230°, 84 g. of solid; 230–270°, 82 g. of semi-solid; 270–300°, 53 g. of solid; residue, 122 g.

Oxidation Experiments.—The only fraction which was closely investigated was that boiling at 135–150° (20 mm.) which should correspond to the biphenyl fraction in the first experiment. A 10g. sample of this material was stirred for eight hours with a boiling solution of 18 g. of potassium permanganate in 1500 cc. of water. After decolorizing the unchanged permanganate by the addition of alcohol, the precipitate was filtered off and washed with ether; the filtrate was shaken with ether, separated, concentrated to 100 cc. and acidified with hydrochloric acid. In this way, 2.0 g. of a mixture of acids melting at 115–180° was obtained. This was recrystallized from carbon tetrachloride, when *p*-phenylbenzoic acid (m. p., 223–224°) was obtained. The ethereal solution was evaporated to dryness, and the residue treated with hydroxylamine hydrochloride and alkali, when 2.0 g. of crude benzophenone-oxime (m. p., 138–140°) was obtained. On recrystallization from alcohol this appeared as long needles melting at 141–142°. Steam distillation of the alkaline mother liquor yielded no biphenyl.

In another experiment, 10 g. of the same fraction was oxidized by means of 30 g. of chromic acid in 75 cc. of glacial acetic acid. The reaction mixture was cooled and poured into 2 liters of water. After standing overnight the crystals were separated and extracted

with 15 cc. of warm petroleum ether (35–60°). The extract deposited 2.3 g. of almost pure benzophenone; m. p., 49°.

Migration of Sodium in Sodium *p*-Tolyl

To 7.7 g. of mercury di-*p*-tolyl in 200 cc. of dry benzene was added 10 g. of metallic sodium in clean shavings. After standing for a month, the brown suspension was decanted from the sodium amalgam and unchanged sodium, and a stream of dry carbon dioxide was passed through the mixture. Reaction began immediately with evolution of heat. After an hour the mixture was warmed on a steam-bath and carbon dioxide passed through the gently boiling solution for four hours, when cold water was added and the upper layer shaken with dilute alkali. The combined aqueous solutions were acidified. The resulting precipitate was found to consist almost entirely of *p*-toluic acid. The weight was 1.64 g. On recrystallization from benzene it melted at 176–177°.

The aqueous filtrate was extracted with benzene; on evaporation to dryness a slightly oily solid remained which on recrystallization from water yielded 1.65 g. of benzoic acid. After sublimation and recrystallization from petroleum ether, and finally from water, it melted at 116–118°. This melting point was unchanged on mixing with authentic benzoic acid. A sample also yielded benzanilide possessing the correct melting point which was unchanged on mixing with benzanilide of known purity.

The first mother liquor from the benzoic acid, which possessed a strong odor of phenylacetic acid, was neutralized and concentrated to a small bulk. Addition of hydrochloric acid yielded an oil which solidified on cooling in ice. After repeated crystallization from water, there was obtained 0.20 g. of phenylacetic acid. This was identified by comparison with authentic phenylacetic acid.

Action of Sodium on Chlorobenzene in the Presence of Dimethylaniline

To a suspension of 520 g. (22.6 g.-atoms) of sodium in 4600 g. of hot dimethylaniline was gradually added, with stirring, 2500 g. (22.2 moles) of chlorobenzene at such a rate that the mixture boiled continually. When the addition was complete, the mixture was allowed to cool, and the slight excess of sodium brought into reaction by adding methyl alcohol, after which 3 l. of water was added. The aqueous solution was separated by siphon, and 1.5 liters more water added to the oily portion. This mixture was then distilled through a column until the temperature of the vapor rose to 99°. The distillate was acidified with hydrochloric acid, and the undissolved oil washed with water and finally with 50% sulfuric acid. The benzene so obtained weighed 845 g. (10.8 moles) and distilled entirely at 79–80°. The residue from which the benzene had been distilled was treated with excess of dil. hydrochloric acid and the insoluble portion warmed with a dil. solution of hydrochloric acid in 30% methyl alcohol. The united acid solutions were neutralized with sodium hydroxide and the resulting oil fractionally distilled under reduced pressure with the use of a column, when the bulk of the unchanged dimethylaniline was recovered in pure condition. The residue from this distillation, amounting to about 85 g., was distilled from a small flask, when it gave the following fractions: 235–271°, 5 g.; 271–282°, 9 g.; 282–292°, 7 g.; 292–296°, 7 g.; 296–304°, 7 g.; 304–308°, 11 g.; 308–315°, 10 g.; 160–190° (16 mm.), 15 g.; 190–280° (16 mm.), 5 g.; residue, 5 g. The last two fractions partially crystallized on cooling; the bulk of the crystallizable material appeared to pass over between 185 and 195° under 16 mm. pressure. The fraction boiling at 304–308° was examined independently; it was soluble in fairly strong acids but was partially precipitated on dilution. A solution in dil. sulfuric acid developed an intense fuchsin color on the addition of dichromate solution; the color was destroyed on warming and an odor of benzaldehyde developed. Benzylmethylaniline was found to behave somewhat similarly, although its solution in dil.

sulfuric acid was considerably less hydrolyzed on further dilution, while on the addition of dichromate a yellow-red color was formed; this, when the mixture was warmed, turned green, and an odor of benzaldehyde developed.

The tar which remained after extraction with dil. hydrochloric acid weighed 960 g. and was found to contain 2.54% of nitrogen, corresponding to 1.75 g. equivalents. On steam distillation it yielded a very small quantity of biphenyl. It was found to be soluble in glacial acetic acid; the solution on exposure to air developed a blue color reminiscent of that obtained by the oxidation of certain derivatives of diphenylamine.

Action of Sodium on *n*-Heptyl Bromide

To 1074 g. of *n*-heptyl bromide (6 moles) heated to about 150° was added sodium in small quantities, with vigorous stirring, at such a rate that the mixture boiled briskly but under control. When about 100 g. of sodium had been added, the mixture became too thick to stir satisfactorily; it was allowed to cool, water was added and the oil separated, dried, and again treated with sodium until no further reaction took place. The unreacted sodium was removed by the addition of alcohol, the salts were dissolved with water and the oil distilled through a small bubbler column; the material distilling up to 101° (after which the temperature rose very rapidly) was collected. The distillate was well washed with water to remove methyl alcohol and treated with a solution of bromine in hydrobromic acid until a permanent excess of bromine was present. After it had been washed with sodium sulfite solution, the resulting liquid was distilled, in the presence of water, through a bubbler column and the distillate collected until only a small proportion of oil passed over with the water. The distillate was separated and the oil shaken repeatedly with concd. sulfuric acid and distilled under atmospheric pressure. It boiled entirely at 96–99° and was practically pure heptane; wt., 50 g. The brominated oil, which was only slightly volatile with steam, was distilled under reduced pressure when it passed over entirely at 103–104° (10 mm.); wt. 79 g. Its properties corresponded to those given in the literature for heptylene bromide.

The residue from which the heptane and heptylene had been distilled was fractionated under reduced pressure, when 395 g. of tetradecane boiling at 115–117° (10 mm.) was obtained. This solidified in a freezing mixture and melted at 4–4.5°. The high-boiling residue on further fractionating yielded a main fraction boiling at 185–195° (10 mm.) and a small quantity of a yellowish oil of still higher boiling range. Analysis of the fraction boiling at 185–195° (10 mm.) showed the presence of 84.3–84.4% of carbon and 14.4–14.6% of hydrogen. It was suspected that the deficiency was due to the presence of oxygenated impurities; the fraction was accordingly repeatedly shaken with concd. sulfuric acid until color was no longer imparted to the acid; it then distilled entirely at 340–345° (corr.). The loss on this purification was very slight.

Anal. Subs., 0.1959, 0.1891: CO₂, 0.6144, 0.5896; H₂O, 0.2630, 0.2538. Calcd. for C₂₁H₄₄: C, 85.04; H, 14.96. Found: C, 85.55, 85.06; H, 15.02, 15.02.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 26.275. Subs., 0.6672, 0.7806, 0.8898; Δt , 0.2290°, 0.2652°, 0.3405°. Calcd.: 296. Found: 289, 292, 290.

Pentadecane from *Iso*-Amyl Bromide.—The high-boiling residue from the preparation of *iso*-decane (by dropping *iso*-amyl bromide slowly onto an excess of sodium on the steam-bath) was distilled under atmospheric pressure and the principal fraction, boiling at 235–245°, repeatedly shaken with concd. sulfuric acid and again distilled, when it passed over almost entirely at 239–242° (corr.).

Anal. Subs., 0.1834. CO₂, 0.5690; H₂O, 0.2503. Calcd. for C₁₅H₃₂: C, 84.81; H, 15.19. Found: C, 84.64; H, 15.27.

Mol. wt. Ebullioscopic method; solvent, benzene. Solvent, 25.949. Subs.,

0.2521, 0.4098, 0.5616; Δt , 0.1175°, 0.1861°, 0.2485°. Calcd.: 212. Found: 215, 221, 232.

The authors desire to express their gratitude to Professor Gomberg at the University of Michigan for permitting some of the experiments and analyses to be carried out in his Laboratory.

Summary

1. The action of sodium upon boiling chlorobenzene leads to the formation of benzene, biphenyl, *o*-diphenylbenzene, *p*-diphenylbenzene (minute amount), triphenylene, *o,o'*-diphenylbiphenyl, together with unidentified resinous and tarry hydrocarbons.

2. The reaction is conveniently interpreted by assuming the intermediate formation of free phenyl and *o*-phenylene radicals.

3. The action of sodium upon *n*-heptyl bromide leads to the formation of heptane, heptylene, tetradecane, a heneicosane of undetermined structure, and hydrocarbons of higher molecular weight. This type of reaction appears to be general for the bromides of primary alcohols.

4. The action of sodium upon chlorobenzene in the presence of an excess of toluene leads to the formation of nearly 50% of benzene; biphenyl is not produced, diphenylmethane, *p*-methylbiphenyl being formed in its stead. The reaction takes an analogous course in the presence of an excess of dimethylaniline, the condensation products containing nitrogen.

5. The constitution of *o*-diphenylbenzene and *o,o'*-diphenylbiphenyl has been confirmed by synthesis.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

SOME CYCLOHEXYL-PHENOLS AND PHENOL ETHERS

BY J. F. BARTLETT¹ WITH C. E. GARLAND

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Considering the many recent developments in the preparation of alkyl and aryl phenols² and the studies made of their germicidal properties, it was decided to prepare some of the cyclohexyl derivatives in order that they might be compared with those already known.

Previous to this time, cyclohexyl-phenol³ is the only derivative of this particular type recorded in the literature. Wuyts prepared this compound

¹ This communication is an abstract of a thesis submitted by J. F. Bartlett, in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry, at West Virginia University.

² The chief contributions have been made by the following investigators. (a) Johnson and Hodge, *THIS JOURNAL*, **35**, 1014 (1913). (b) Johnson and Lane, *ibid.*, **43**, 348 (1921). Leonard, *J. Am. Med. Assoc.*, **83**, 2005 (1924). (c) Dohme, Cox and Miller, *THIS JOURNAL*, **48**, 1688 (1926). (d) Klarman, *ibid.*, **48**, 791, 2358 (1926).

³ Wuyts, *Bull. soc. chim. Belg.*, **26**, 304 (1912).

by condensing cyclohexanol with a large excess of phenol in the presence of toluene-4-sulfonic acid. The melting point recorded is 128°.

Applying the method Klarmann^{2d} used in similar reactions, cyclohexyl chloride was condensed with resorcinol, anisole and phenetole in the presence of anhydrous aluminum chloride. For the preparation of cyclohexyl-phenol, Klarmann's modification of the method employed by Liebmann⁴ was used. Cyclohexyl chloride was condensed with phenol in the presence of anhydrous aluminum chloride. It was also prepared from cyclohexyl-anisole by hydrolysis with constant-boiling hydrobromic acid. In each case the compound was the same as that prepared by Wuyts, as indicated by the melting point.

The phenol coefficients⁵ of cyclohexyl-resorcinol and cyclohexyl-phenol were determined. The solubility of cyclohexyl-resorcinol in distilled water is 51 mg. per 100 cc. at 25°. Using this solution, a phenol coefficient of 23-27 was found. Apparently the cyclic structure of the side chain reduces the phenol coefficient, as compared with that of *n*-hexyl-resorcinol (46-56), to near that of the *isohexyl*-resorcinol recorded by Dohme, Cox and Miller, which is given as 27. The solubility of cyclohexyl-phenol in distilled water is 6 mg. per 100 cc. at 25°. At this concentration no germicidal properties were indicated.

Work in the field of cyclohexyl-phenols and derivatives is being continued.

Experimental Part

Cyclohexyl-resorcinol. $C_6H_5(C_6H_{11})(OH)_2(1,2,4)$.—Cyclohexyl chloride was prepared by treating cyclohexanol with concd. hydrochloric acid, and refluxing slowly while dry hydrogen chloride was passed through the mixture, in order to increase the yield. This was continued for a period of about three hours. The upper layer of cyclohexyl chloride was separated, washed first with dil. sodium carbonate solution and then with water. After drying with calcium chloride it was subjected to fractional distillation and a yield of 65% was obtained; b. p., 141-143° at atmospheric pressure.

For the condensation of cyclohexyl chloride with resorcinol a two-liter flask was fitted with a reflux condenser, dropping funnel and a mercury-seal stirrer. Ninety g. of resorcinol dissolved in 450 cc. of freshly distilled nitrobenzene, together with 18 g. of aluminum chloride (anhydrous) was placed in the flask. Seventy-seven g. of cyclohexyl chloride was slowly added while the reaction mixture was rapidly stirred and slowly heated to 70° on the water-bath. After about four hours, when the hydrogen chloride was practically all liberated, the contents of the flask were poured onto ice and allowed to cool. A quantity of ether equal in volume to the dark oily liquid was added and this solution extracted with 10% sodium hydroxide until it produced no further coloration. The alkaline solution was made acid with hydrochloric acid and steam distilled to remove traces of nitrobenzene. On cooling, white, crystalline plates of cyclohexyl-resorcinol separated, together with a quantity of tarry material which settled to the bottom of the flask. On standing for several days, the dried crystals turned slightly

⁴ Liebmann, *Ber.*, 14, 1842 (1881).

⁵ Phenol coefficients were determined according to the method of the Hygienic Laboratory, by Dr. R. S. Spray of the West Virginia University School of Medicine. For his cooperation the thanks of the authors are due.

brown and a solution of the substance in water, on long standing, developed a fluorescence. In alcohol and ether the substance is readily soluble, and the sodium salt is soluble in water; m. p., 124–125°; yield, about 5%.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.75, 74.43; H, 8.28, 8.87.

Cyclohexyl-anisole. $C_6H_4(C_6H_{11}).OCH_3(1,4)$.—Forty-two g. of anisole was condensed with 30 g. of cyclohexyl chloride in the presence of 6 g. of anhydrous aluminum chloride. The procedure was the same as with cyclohexyl-resorcinol except that an additional solvent was not used. The oily liquid from the reaction was dried and subjected to distillation at 16 mm. pressure. The distillation commenced at 134° and continued to 200°. The distillate was then subjected to fractional distillation at 16 mm. and analyzed. This, together with the conversion to the free phenol, indicated that the larger fraction which came over between 146 and 148° was the cyclohexyl-anisole. This material solidified when placed in an ice-bath but remained liquid at room temperature. A very small amount of higher-boiling fraction was obtained which has not yet been identified; yield of 146–148° fraction, 15–20%; d_4^{20} , 1.0209; d_4^{25} , 1.0004; n_D^{25} , 1.5305; molecular refraction: calcd. 58.07, found: 58.71. The molecular weight was determined by the cryoscopic method, using benzene as a solvent.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.33, 82.22; H, 9.70, 9.55.

Mol. wt. Calcd. for $C_{13}H_{18}O$: 190.14. Found: 184.8.

Cyclohexyl-phenetole. $C_6H_4(C_6H_{11}).OC_2H_5(1,4)$.—Thirty-four g. of phenetole was condensed with 30 g. of cyclohexyl chloride in the presence of 6 g. of anhydrous aluminum chloride, the general procedure in this case being the same as that described above. The condensation product on distillation gave one principal fraction 155–157° (16 mm.). After standing for several days it mostly solidified to very small prismatic needles; yield, 12%; n_D^{25} , 1.5262.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.41, 82.17; H, 10.10, 9.80.

Cyclohexyl-phenol. $C_6H_4(C_6H_{11}).OH(1,4)$.—*Method I.* This phenol was obtained from cyclohexyl-anisole by hydrolysis with constant-boiling hydrobromic acid mixed with glacial acetic acid. It was purified by recrystallization of the sodium salt from water solution. The sodium salt on decomposition with acid gave a white, crystalline solid; m. p., 128°; yield, 14%.

Method 2. Cyclohexyl-phenol was also prepared by condensing cyclohexyl chloride with phenol in the presence of fused zinc chloride. Ninety g. of phenol was condensed with 118 g. of cyclohexyl chloride in the presence of 118 g. of fused zinc chloride. The reaction mixture was heated in a water-bath until the evolution of hydrogen chloride could no longer be observed. It was then poured onto ice and from the oily liquid the sodium salt of the phenol was obtained by alkaline extraction. The phenol was further purified as under the first method; yield, 20%; m. p., 128°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 81.79; H, 9.16. Found: C, 81.67; H, 9.11.

The benzoyl ester of the cyclohexyl-phenol was prepared by the Schotten-Baumann reaction. Recrystallization from alcohol gave a white, crystalline solid; m. p., 114–114.5°.

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 81.38; H, 7.19. Found: C, 81.04, 80.96; H, 7.20, 7.21.

Summary

1. Four new compounds have been prepared; cyclohexyl-resorcinol, cyclohexyl-anisole, cyclohexyl-phenetole and the benzoyl ester of cyclo-

hexyl-phenol. The properties of these compounds have been determined. Cyclohexyl-phenol, which has been prepared previously, was obtained by two new methods.

2. Cyclohexyl-phenol was not found to have any germicidal properties in water solution because of its limited solubility. Cyclohexyl-resorcinol gave a phenol coefficient of 24-27.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SELECTIVE REDUCTION OF FURFURACROLEIN BY MEANS OF PLATINUM-OXIDE PLATINUM BLACK AND HYDROGEN. XVI¹

BY R. H. BRAY² WITH ROGER ADAMS

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In a previous paper it was shown that aldehydes³ could not be reduced to alcohols with hydrogen and platinum-oxide platinum black unless some promoter such as a ferrous salt was present. As these promoters for the reduction of aldehydes are poisons toward the reduction of olefins, the study of the reduction of α,β unsaturated aldehydes,⁴ in particular cinnamic aldehyde and citral, resulted in the discovery that by using a ferrous salt, together with a small amount of zinc salt, it was possible to reduce quantitatively the aldehyde group to a primary alcohol without affecting the olefin linkages. Cinnamyl alcohol and geraniol, respectively, were produced.

Furfural⁵ was like other aldehydes and the catalytic reduction with platinum-oxide platinum black and hydrogen would not take place unless ferrous salt or some such promoter was present. The primary product was furyl carbinol formed upon the absorption of one molecular equivalent of hydrogen. If the reduction was allowed to go until no more absorption of hydrogen took place, ordinarily slightly over four molecular equivalents of hydrogen were absorbed, and there resulted a mixture of tetrahydro-furyl carbinol, pentane-diol-1,2, pentane-diol-1,5, and a small amount of *n*-amyl alcohol, the latter three substances being produced by scission of the ring.

In the present investigation the work on selective reduction has been

¹ (a) For previous papers in this field, see Adams, Cohen and Rees, *THIS JOURNAL*, **49**, 1093 (1927) (footnote 1) for references to the first thirteen articles; (b) also Hiers and Adams, *ibid.*, **49**, 1099 (1927).

² This communication is an abstract of a portion of a thesis submitted by R. H. Bray in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

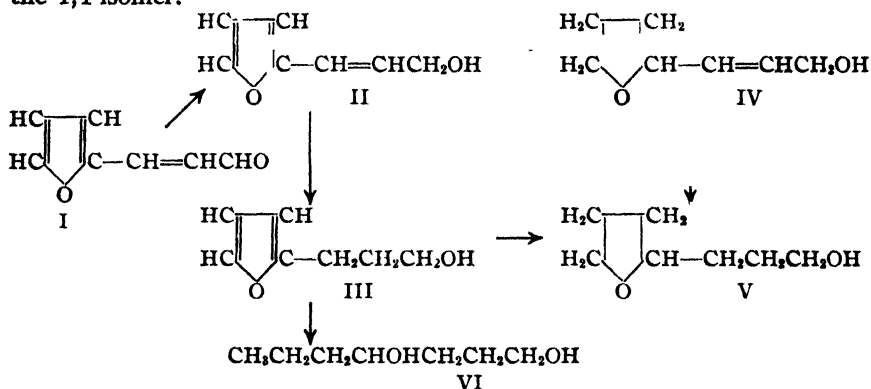
³ (a) Carothers and Adams, *ibid.*, **45**, 1071 (1923); (b) **46**, 1675 (1924).

⁴ (a) Tuley and Adams, *ibid.*, **47**, 3061 (1925); (b) Adams and Garvey, **48**, 477 (1926).

⁵ Kaufman and Adams, *THIS JOURNAL*, **45**, 3029 (1923).

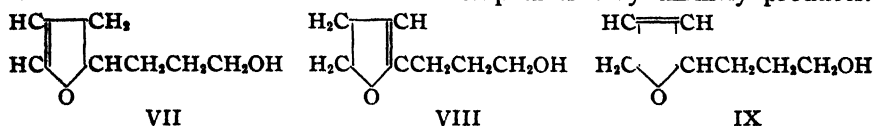
extended to furfuracrolein (I) which combines certain conditions present in furfural and in α,β unsaturated aldehydes. This compound, as might be expected, could not be reduced unless a promoter was present. The presence of ferrous sulfate caused the absorption of hydrogen to take place although, as in the case of the cinnamic aldehyde, the reaction did not stop after one molecular equivalent had reacted, but more hydrogen was absorbed to a maximum of 4.3–4.4 molecular equivalents. If the reaction mixture was distilled after one molecular equivalent of hydrogen was absorbed no pure product was obtained. When a small amount of zinc acetate, in addition to the ferrous salt was present, however, the absorption of hydrogen stopped completely after one molecular equivalent reacted and a single product resulted—furyllallyl alcohol (II).

An attempt was made to isolate pure products after two molecular equivalents of hydrogen had been absorbed, using merely the ferrous salt to promote the reaction, but the results were unsuccessful. After the absorption of three molecular equivalents of hydrogen, two pure products could be separated from the reaction mixture by distillation, furylpropyl alcohol (III) and tetrahydrofuryllallyl alcohol (IV), the former in the larger quantities. Finally, after all of the hydrogen was absorbed which would react, a good yield of tetrahydrofurylpropyl alcohol (V) resulted, with small amounts of a heptane-diol (VI), which was probably the 1,4-isomer.



Obviously the mechanism consists first in the absorption of hydrogen to reduce the aldehyde group. This is followed by the reduction either of the olefin groups in the furane nucleus or of the olefin linkage in the side chain. Since the yield of tetrahydrofuryllallyl alcohol was much smaller than that of the furylpropyl alcohol, the tendency for the aliphatic olefin linkage to reduce is greater than of the ring olefin linkages. The furylpropyl alcohol is then reduced for the most part to the tetrahydro derivatives, but a little of it, as with furylcarbinol, is reduced with splitting of the oxygen ring and formation of a diol.

It was assumed that tetrahydrofurylallyl alcohol is actually the substance which was obtained and not one of the possible isomers. Although there are five isomeric compounds which agree with the analyses, the *cis* or *trans* form of the tetrahydrofurylallyl alcohol and three isomeric dihydrofuryl propyl alcohols (VII, VIII, IX), the extreme difficulty in isolation of a dihydrofuryl derivative by any method of reduction of a furane derivative renders the latter compounds very unlikely products.



Whether the compound in hand is the *cis* or *trans* modification of tetrahydrofurylallyl alcohol has not been determined.

The heptane diol isolated is probably the 1,4-isomer, as can be seen by comparing its constants and those of its derivatives with the 1,7-isomer prepared by another method.⁶

TABLE I
PHYSICAL CONSTANTS OF GLYCOLS

	Heptane-diol 1,4	Heptane diol 1,7
Glycol	B p , 126 5-128 5° (4 mm) , 240-245° (750 mm) , n_D^{25} , 1 4510, d_{20}^{20} 0 9559	B p , 262° (atm)
Diacetate	B p , 113-113 5° (1 mm) , 249-252° (748 mm) , n_D^{25} , 1 4268, d_{20}^{20} 0 9934, d_0^0 , 1 0135	B p , 274° (atm) , d_0^0 , 1 0219
Phenylurethan	Oil	M p , 134°
α -Naphthylurethan	M p , 81-82°	

The lower boiling point would indicate the 1,4-isomer, since in isomeric straight-chained glycols the one with the hydroxyl groups closer together invariably boils lower. Moreover, the indices of refraction of glycols increase as the hydroxyl groups are situated further apart. The values are of the same order for 1,2-glycols, for 1,5-glycols, etc., regardless of the number of carbon atoms in the molecule. From the data given below, therefore, the indications are for the 1,4-isomer.

TABLE II
INDICES OF REFRACTION OF GLYCOLS

Compounds	n_d
Pentane-diol 1,2 ^a	1 4412
Pentane-diol 1,5 ^a	1 4499
Heptane-diol 3,4 ^b	1 4420
Heptane-diol new	1 4510
Heptane-diol 1,5 ^b	1 4571
Nonane-diol 4,5 ^b	1 4476
Nonane-diol 1,5 ^b	1 4560

^a Ref. 5

^b Pierce and Adams, *THIS JOURNAL*, 47, 1098 (1925)

⁶ R. Dionneau, *Ann chim*, [9] 3, 248 (1915).

Acetates and α -naphthylurethan derivatives of the various compounds isolated were prepared and identified.

Experimental

Materials.—The platinum oxide was prepared according to the method of Adams and Shriner⁷ from C. P. chloroplatinic acid.

The furfuracrolein was prepared by the method of Konig and Hey⁸ by condensation of furfural with acetaldehyde. In order to purify the product, fractional distillation under diminished pressure was found much more satisfactory than steam distillation followed by crystallization. It was absolutely necessary that the material be freshly distilled before the reduction was started or else the reaction took place only very slowly or not at all.

Reduction of Furfuracrolein (I).—In a typical run 0.2 g. of platinum oxide, 0.00002 mole of ferrous sulfate, 100 cc. of alcohol and 24.4 g. of furfuracrolein were used. The platinum oxide was reduced to platinum black in half of the alcohol, then the ferrous sulfate, the furfuracrolein and the rest of the alcohol were added. The reduction was carried out under 2.5–3 atmospheres' pressure with hourly reactivations with air or oxygen for the first seven hours and then occasional reactivations thereafter. The time for the complete reduction, during which 4.2–4.4 molecular equivalents of hydrogen were absorbed, was approximately 24 hours.

In the preparation of furylallyl alcohol, 0.00003 mole of zinc acetate and 0.0002 mole of ferrous sulfate were used in place of the amount of ferrous sulfate in the typical run just described. The reduction was thus slowed down and it practically stopped after one molecular equivalent of hydrogen had been absorbed. The time for this reduction was about 9.5 hours as compared with 4.5 hours for the absorption of one molecular equivalent when no zinc salt was added.

The products were isolated by means of fractional distillation under diminished pressure. The alcohols with unsaturated side chains always yield a certain amount of red, resinous residue when distilled, indicating partial decomposition or polymerization.

Furylallyl Alcohol (II).—Upon the reduction of 24.4 g. of furfuracrolein in presence of iron and zinc salts as described above until one molecular equivalent of hydrogen was absorbed, 19 g. of pure product was isolated. The furylallyl alcohol boils at 108–110° at 4 mm.; n_D^{27} , 1.5520; d_{20}^{20} , 1.1439. Upon distillation it decomposes somewhat and always leaves a high-boiling residue. On standing it turns yellow, then red and finally thickens. By the action of acetic anhydride no ester was obtained, as decomposition apparently took place.

Anal. Subs., 0.1480: CO₂, 0.3668; H₂O, 0.0890. Calcd. for C₇H₈O₂: C, 67.72; H, 6.50. Found: 67.61; 6.73.

α -Naphthyl Urethan of Furylallyl Alcohol.—The α -naphthyl urethan derivative was prepared according to the directions of Bickel and French⁹ from the alcohol and α -naphthyl isocyanate. The product crystallizes from ligroin in white rosetts. When pure it melts at 93–93.5°.

Anal. Subs., 0.1000: 4.60 cc. of 0.0714 N NaOH. Calcd. for C₁₈H₁₈O₂N: N, 4.78. Found: 4.60.

Furylpropyl Alcohol (III).—From a reduction of furfuracrolein using ferrous sulfate and stopping the reaction after approximately 3 molecular equivalents of hydrogen were absorbed, there was obtained by fractionation two products. One, the lower-distilling,

⁷ Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).

⁸ Konig and Hey, *Frdl.*, **13**, 110 (1923).

⁹ Bickel and French, *THIS JOURNAL*, **48**, 747 (1926).

which proved to be furylpropyl alcohol, boils at 90–91° at 4 mm.; 201–208° at 747 mm.; n_D^{25} , 1.4760; d_4^{20} 1.0613. The yield was approximately 50 per cent. of the calculated amount. The product gradually turns yellow on standing.

Anal. Subs., 0.1584: CO₂, 0.3859; H₂O, 0.1158. Calcd. for C₇H₁₀O₂: C, 66.63, H, 7.99. Found: 66.46, 8.18.

α -Naphthyl Urethan of Furylpropyl Alcohol.—It forms white crystals from ligroin, m. p., 49°.

Anal. Subs., 0.1500: 7.06 cc. of 0.0714 N NaOH. Calcd. for C₁₈H₁₉O₂N: N, 4.71. Found: 4.71.

Furylpropyl Acetate.—A mixture of 10 cc. of alcohol and an excess of acetic anhydride was refluxed for 3.5 hours. The pure ester boils at 92° at 2 mm.; 217–218° at 747 mm.; n_D^{25} , 1.4553; d_4^{20} 1.0601. It turns yellow on standing.

Anal. Subs., 0.1410: CO₂, 0.3299; H₂O, 0.0927. Calcd. for C₉H₁₂O₂: C, 64.26; H, 7.19. Found: 63.83, 7.36.

Tetrahydrofurylallyl Alcohol (IV).—The higher-boiling material obtained after separating the furylpropyl alcohol proved to be tetrahydrofurylallyl alcohol. It boils at 100–101° at 4 mm.; n_D^{25} , 1.4675; d_4^{20} , 1.0317. The yield of pure product was approximately 10 per cent. It turns red on standing. It was impossible to obtain solid derivatives with α -naphthyl isocyanate, phenyl isocyanate, or 3,5-dinitrobenzoyl chloride.

Anal. Subs., 0.1613: CO₂, 0.3853; H₂O, 0.1360. Calcd. for C₇H₁₀O₂: C, 65.59; H, 9.44. Found: 65.17, 9.43.

Tetrahydrofurylallyl Acetate.—The acetate boils at 90–91° at 2 mm.; n_D^{25} , 1.4468; d_4^{20} , 1.0374. It turns yellow-orange on standing.

Anal. Subs., 0.1168: CO₂, 0.2710; H₂O, 0.0845. Calcd. for C₉H₁₄O₂: C, 63.50; H, 8.29. Found: 63.30, 8.10.

Tetrahydrofurylpropyl Alcohol (V).—When the reductions in the presence of a little ferrous sulfate were run to completion with the absorption of 4.2–4.4 molecular equivalents of hydrogen, the chief product of reaction was tetrahydrofurylpropyl alcohol in yields of about 60 per cent. It boils at 106–107° at 2 mm.; 221° at 747 mm.; n_D^{25} , 1.4540; d_4^{20} , 1.0032. The higher-boiling fraction was a heptane-diol described below.

Anal. Subs., 0.1158: CO₂, 0.2732; H₂O, 0.1126. Calcd. for C₇H₁₄O₂: C, 64.57; H, 10.84. Found: 64.36, 10.88.

3,5-Dinitrobenzoate of Tetrahydrofurylpropyl Alcohol.—By warming molecular equivalents of the alcohol and 3,5-dinitrobenzoyl chloride on a water-bath, then adding water, the ester was obtained which, on purification from dil. alcohol, melts at 65.5–66°.

Anal. Subs., 0.2000: 17.2 cc. of 0.0714 N NaOH. Calcd. for C₁₄H₁₆O₇N₂: N, 8.64. Found: 8.60.

Tetrahydrofurylpropyl Acetate.—This product boils at 99° at 2 mm.; 228.5–229° at 750 mm.; n_D^{25} , 1.4380; d_4^{20} , 1.0207.

Anal. Subs., 0.1983: CO₂, 0.4546; H₂O, 0.1673. Calcd. for C₉H₁₆O₂: C, 62.75; H, 9.37. Found: 62.54, 9.44.

Heptane-diol 1,4 (VI).—The high-boiling fraction from the complete reduction of furfuracrolein proved to be a heptane-diol and was obtained in about 10 per cent. yields. It boils at 126.5–128.5° at 4 mm.; 240–245° at 750 mm.; n_D^{25} , 1.4510; d_4^{20} , 0.9559. It is completely miscible in water.

Anal. Subs., 0.1894: CO₂, 0.4423; H₂O, 0.2039. Calcd. for C₇H₁₆O₂: C, 63.58; H, 12.20. Found: 63.71, 12.05.

α -Naphthyl Urethan of Heptane-diol.—This product on crystallization from ligroin melts at 81–82°.

Anal. Subs., 0.1000: 5.60 cc. of 0.0714 *N* NaOH. Calcd. for $C_{21}H_{26}O_4N_2$: N, 5.95. Found: 5.60.

Heptane-diol Diacetate.—The substance boils at 113–113.5° at 1 mm.; 249–252° at 748 mm.; n_D^{25} , 1.4268; d_{20}^{20} , 0.9934; d_4^{20} 1.0135.

Anal. Subs., 0.1019: CO_2 , 0.2280; H_2O , 0.0876. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.28. Found: 61.05, 9.62.

Summary

1. The reduction of furfuracrolein in alcohol solution was carried out using platinum-oxide platinum black as a catalyst and a little ferrous sulfate as a promoter. After the absorption of 3 molecular equivalents of hydrogen, there was isolated furylpropyl alcohol and tetrahydrofurylallyl alcohol. After absorption of 4.2–4.4 molecular equivalents of hydrogen, the maximum amount taken up, there was obtained tetrahydrofurylpropyl alcohol and a heptane-diol.

2. An attempt to isolate products after the absorption of one molecular equivalent or two molecular equivalents of hydrogen was unsuccessful. If the reduction was carried out in the presence of ferrous sulfate and zinc acetate, however, the reduction stopped automatically after one molecular equivalent of hydrogen had been absorbed and pure furylallyl alcohol was readily obtained.

3. The acetates of many of the alcohols were prepared and the α -naphthyl urethans of some of them.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORY OF THE DEPARTMENT OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO THE ARTICLE OF THIS TITLE BY SMITH, BOORD, ADAMS AND PEASE

BY HENRY DE LASZLO¹

RECEIVED JUNE 8, 1927

PUBLISHED AUGUST 5, 1927

The ultraviolet absorption spectra of a large number of colorless aliphatic and aromatic compounds have been studied by Henri and his co-workers. One of the main results of this very careful examination was that while benzene possesses some very well marked bands in the region $\lambda 2600 \text{ \AA.} - \lambda 2400 \text{ \AA.}$, the saturated cyclic and open-chain aliphatic hydrocarbons are transparent in this portion of the spectrum. Even decahydronaphthalene² absorbs only from 2300 \AA. downwards. The intro-

¹ Research Associate, Department of Physics, Massachusetts Institute of Technology.

² De Laszlo, *Proc. Roy. Soc. (London)*, 111A, 376 (1926).

duction of one double bond in an otherwise saturated molecule gives rise to only broad absorption bands both in vapor and in solution.

All saturated aliphatic alcohols so far examined show no absorption above $\lambda 2400 \text{ \AA.}$; below this they all have a very broad absorption band, the position of whose maximum varies from $\lambda 2200 \text{ \AA.}$ to $\lambda 2350 \text{ \AA.}$, passing from methyl to butyl alcohol. The introduction of a halogen does not, as a rule, alter the general appearance of the spectrum, but if any bands were present in the original substance, these will be displaced toward the visible³ by an amount depending on the size of the molecule. Pure ethyl ether shows no absorption above 2100 \AA. , even the liquid being perfectly transparent in a thickness of 40 mm. In fact, ethyl ether and hexane have been used as solvents for the past years in the measurement of ultraviolet absorption spectra.⁴ The higher aliphatic ethers will show a slight shift toward the red, the absorption limit depending on the number of CH_2 groups in the molecule.

Benzene vapor possesses a very characteristic absorption spectrum consisting of more than 400 lines and band-heads. Of the 200 substances possessing a measurable absorption that have been examined by Henri and his pupils, no two were found to have identical spectra. Nor is this in any degree probable when one considers the very complicated mechanism that gives rise to these spectra.

If, therefore, the work of Smith, Boord, Adams and Pease, published in *THIS JOURNAL*, 1927, page 1335, were correct, then all previous experimental data would be false, which is hardly possible. These four authors find absorption spectra identical to that of benzene for the following substances: cyclohexene, ethyl ether, ethylene chlorohydrin and methyl-*n*-amyl ether. These, however, all fall into the categories mentioned above and will, therefore, show no absorption between $\lambda 2600 \text{ \AA.}$ and $\lambda 2400 \text{ \AA.}$

In order to confirm this, we have examined ethylene chlorohydrin in vapor and in liquid phase.

Experimental Work

One hundred grams of Eastman Kodak Company ethylene chlorohydrin was rapidly distilled in an all-glass Witmer fractionating apparatus. The portion boiling from 128.7 to 128.8° at 764 mm. was collected. This fraction was colorless and possessed only a very faint alcoholic odor. The absorption spectrum of the vapor was then photographed in a layer 15 cm. thick at temperatures varying from 50 to 110° by steps of 10° . No appreciable absorption above 2250 \AA. was to be seen.

The pure liquid was examined in thicknesses of $\frac{1}{10}$ to 5 mm. Con-

³ De Laszlo, *Proc. Roy. Soc.*, (London), 111A, 359 (1926).

⁴ Castille and Henri, *Bull. soc. chim. biol.*, 6, 299-304 (1924).

tinuous absorption below 2300 Å. was observed for a layer 4 mm. thick. A detailed description of the technique will be given in a later article. Hence, it is clear that pure ethylene chlorohydrin does not absorb appreciably above 2300 Å., and then only in a perfectly continuous manner.

Results

It is obvious, therefore, that in every case mentioned by these authors benzene vapor was present. To show how strong the bands of benzene are, we may state that at a pressure of 0.01 mm. the following five band-heads are still visible as five lines: $\lambda 2589.03$ Å., $\lambda 2528.57$ Å., $\lambda 2471.03$ Å., $\lambda 2415.91$ Å., $\lambda 2363.55$ Å. In other words, it has been found that a mass of benzene as small as $1/10,000$ mg. will still give rise to its characteristic band-heads.

All this goes to show how rigorous must be the purification of those compounds whose absorption spectra are to be determined. Thus, in the case of the substances in question, the distillation should be conducted in an all-glass apparatus with an efficient distilling column of the type developed by Witmer.⁵ The boiling-point range should be $\pm 1/10^\circ$ and this fraction should consist of a major portion of the sample. Wherever possible it has been found best to follow this with three or four crystallizations out of optically pure hexane⁴ at about -100° . Chemical purification is also advantageous when possible, as shown in the case of cyclohexane where the benzene present was removed by washing with sulfuric acid. The apparatus for vaporizing and photographing the substance must, of course, be scrupulously clean and is best made entirely of fused quartz so that drastic cleansing with sulfuric and chromic acids may be resorted to.

Aside from the fact that these authors erroneously ascribe the ultra-violet benzene bands to other compounds than benzene, their attempted correlation of the vibrational constants with those of the infra-red bands observed by Ellis⁶ seems open to serious objections; for although the theory of polyatomic band spectra is not yet sufficiently developed to account for the empirical form of Henri's equation for band-heads, involving two sets of integral "quantum numbers," it is probable that the observed vibrational constants are characteristic of the *excited* electronic state. At room temperature we should expect only transitions from the zero vibrational level of the initial (normal) state to be of appreciable intensity in absorption. On the other hand, the infra-red vibration-rotation bands involve only the vibrational terms of the *normal* state, and thus should not in general give constants related to those of the ultra-violet absorption bands. The only satisfactory correlation of electronic

⁵ Dis Zürich Eidg. Tech Hochschule, 1924.

⁶ Ellis, *Phys. Rev*, 27, 298 (1926).

bands with those of the infra-red seems at present to be that given by Birge,⁷ in which the constants of the normal state of carbon monoxide, determined from the emission spectrum, are successfully used to compute the positions of the three strongest vibration-rotation bands.

The agreements which are shown in Table II, p. 1344, of the article under discussion are certainly not convincing. The band of longest wave length in the series found by Ellis is that at 6.7μ , which he interprets as the "fundamental" ($0 \rightarrow 1$) band. The remaining "observed values" in the table should not exist on this interpretation (unless they are combination bands) and, since they are not included by Ellis, must be of small intensity. However, it is precisely the bands of shorter wave length than 6.7μ which require unreasonably large values of n_1 and n_2 for representation by Henri's formula. In fact, with an equation of two independent variables, any other values for the coefficients may be used and still, with suitable assignments of n_1 and n_2 , be made to yield wave lengths which agree as well as those shown. As an illustration we may assume the relation $\nu n = 1000n_1 + 100n_2$ and find the following agreements.

TABLE I

n_1	n_2	(obs.)	("calcd.")	("calcd." Smith, etc.)
15	18	0.760	0.758	0.760
13	10	.835	.834	.831
12	10	.913	.910	.910
11	12	1.022	1.021	1.022
9	5	1.172	1.177	1.166
8	7	1.379	1.370	1.370
7	11	1.695	1.695	1.684
5	4	2.16	2.17	2.19
5	10	2.49	2.50	2.45
4	4	2.75	2.78	2.74
4	9	3.25	3.23	3.28
2	2	5.40	5.56	5.53
2	5	6.7	6.7	6.6

We do not agree, therefore, that the authors have "thus disposed of the physical significance of the ultraviolet absorption of these compounds." There can be no doubt, however, that the use of two sets of integers covering a limited range of small values is significant as permitting a satisfactory representation of a large number of the ultraviolet benzene bands, and also that the single parabolic series of infra-red bands bears a striking resemblance to the analogous bands of diatomic molecules.

Again, if the experimental data and theoretical conclusions given by these authors are correct, namely, that the C-H linkage gives rise to this identical band structure in four different cases, why then are they not obtained for cyclohexane which contains plenty of these linkages?

⁷ Birge, *Phys. Rev.* **28**, 1157 (1926).

Summary

1. It has been proved that the experimental results of Smith, Boord, Adams and Pease are erroneous on the following grounds.

(a) Past experience has shown that bodies of the type examined show only continuous absorption from 2350 Å. to 2000 Å.

(b) The absorption of two out of the four substances concerned has been measured and no evidence of a benzene-like structure such as is claimed has been found.

(c) It has been pointed out that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results reported by these authors.

2. Their theoretical deductions have also been shown to be unconvincing.

3. It has been pointed out that in this type of work absolute purity of the compounds examined and cleanliness of the apparatus used are essential.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

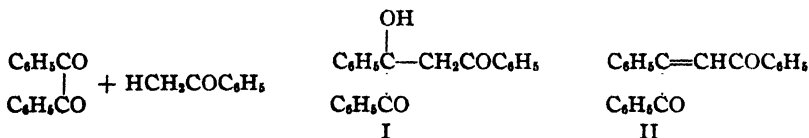
THE SYNTHESIS OF ALPHA,BETA-DIACYLSTYRENES AND THEIR REACTION WITH HYDROGEN BROMIDE

BY CHARLES F. H. ALLEN AND HARRY B. ROSENER

RECEIVED JUNE 13, 1927

PUBLISHED AUGUST 5, 1927

Japp and his co-workers¹ found that in the presence of alcoholic potassium hydroxide, benzil reacts with acetophenone and forms first an addition product (I), and finally an unsaturated diketone (II), which they called anhydracetophenone benzil or α,β -dibenzoylstyrene.²



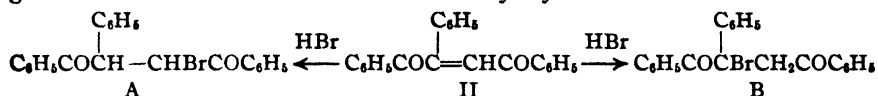
We have found that many other dibenzoylstyrenes can be made in this manner, but that the reaction is not general. It was possible to substitute for the acetophenone used by Japp a number of other methyl ketones which had alkyl groups or chlorine atoms in the nucleus, while with other closely related methyl ketones the reaction failed. Thus, di-

¹ Japp and co-workers, *J. Chem. Soc.*, (a) 47, 35 (1885); (b) 51, 430 (1887); (c) 53, 184 (1888); (d) 57, 662 (1890); (e) 71, 1138 (1897); *Ber.*, (f) 18, 187 (1885); (g) 21, 2933 (1888).

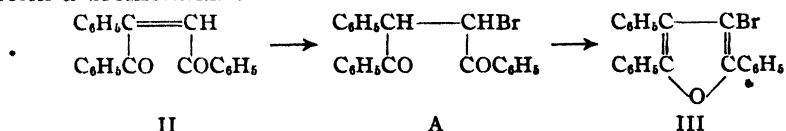
² It might better be called phenyldibenzoylethylene, but the naming of compounds substituted in one benzoyl group seems clearer if they are considered as derivatives of styrene.

acylstyrenes were made successfully by condensing benzil with $\text{CH}_3\text{CO}\cdot\text{C}_6\text{H}_5$, $\text{CH}_3\text{COC}_6\text{H}_4\text{CH}_3$ (4), $\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)_2$ (3,4), $\text{CH}_3\text{COC}_6\text{H}_4\text{OCH}_3$ (4), $\text{CH}_3\text{COC}_6\text{H}_3(\text{OCH}_3)_2$ (3,4), $\text{CH}_3\text{COC}_6\text{H}_4\text{Cl}$ (4), $\text{CH}_3\text{COC}_6\text{H}_4\text{Br}$ (4) and $\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)(3)\text{Cl}$ (4). The reaction was tried unsuccessfully with $\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)_2$ (2,4), $\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)_2$ (2,5), $\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)(2)\text{-(i-C}_4\text{H}_7)$ (5), $\text{CH}_3\text{COC}_6\text{H}_3\text{Cl}(2)(\text{CH}_3)$ (5) and $\text{CH}_3\text{COC}_6\text{H}_2(\text{CH}_3)_3$ (2,4,5), the benzil being recovered unchanged. A comparison of the results shows that the reaction fails whenever there is a substituent in the *ortho* position of the acetophenone. This is a peculiar effect of hindrance for which at present there appears to be no adequate explanation. It seems to imply that some kind of addition reaction or complex formation involving the carbonyl group of the methyl ketone must precede condensation.

The styrene derivatives which are obtained in this manner have an ethylenic linkage that is conjugated with two carbonyl groups. They could therefore add substances of the type HX in two ways. Thus, hydrogen bromide could combine with dibenzoylstyrene to form either A or B.



In a series of papers dealing with addition reactions of α,β unsaturated ketones, Kohler³ has shown that while 1:4 addition is prevented if there are two substituent groups in the beta position to the carbonyl group, it takes place readily with compounds having alpha substituents, but at a slower rate than when both positions are unsubstituted. If this relation holds for substances containing conjugated systems of the type in the dibenzoylstyrenes, then the addition product with hydrogen bromide should be A. This is a 1:4 diketone with hydrogen atoms alpha to each carbonyl group; it would, therefore, be expected to lose water easily and form a bromofurane.



We have found that when α,β -dibenzoylstyrene in chloroform or acetic acid solution is treated with hydrogen bromide, the bromofurane (III) separates in nearly the calculated yield. The presence of the third phenyl group appears to favor ring closure because both the saturated bromoketone and the bromofurane can be isolated when hydrogen bromide is added to a chloroform solution of dibenzoylethylene, the corresponding unsubstituted diketone.⁴ We have also found that this transformation

³ Kohler, *Am. Chem. J.*, 1905-1911.

⁴ Paal and Schulze, *Ber.*, 35, 172 (1902). Pratt, *Dissertation*, Harvard University, 1927.

of an unsaturated diketone into a bromofurane is quite general, as it took place with all but one of the diacystyrene derivatives.

Experimental Part

A. Condensation of Benzil and Substituted Acetophenones.—The general directions are as follows. One-twentieth mole of benzil and one-twentieth mole of the ketone are warmed with 5 cc. of methyl alcohol until dissolved. A solution of 0.2 g. of sodium in 25 cc. of methyl alcohol is added, the mixture kept near the boiling point for a few minutes and then allowed to stand overnight. The product is filtered off, washed with dil. alcohol until free from alkali, and recrystallized by dissolving in the smallest possible amount of boiling chloroform and adding an equal volume of methyl alcohol. Glacial acetic acid may also be used for recrystallization. The diketones form small, light yellow prisms almost insoluble in the alcohols and ether, sparingly soluble in acetone, but easily soluble in hot chloroform, acetic anhydride, and acetic acid. Yields, 80–85%.

TABLE I
DERIVATIVES OF α,β -DIBENZOYLSTYRENE

No.	Ketone used ^a (acetophenone derivation)	M. p., °C.	Formula	Analyses			
				Calcd., C	% H	Found, C	% H
II	Acetophenone	129					
IV	4-Methyl-	158	$C_{23}H_{18}O_2$	84.7	5.5	84.3	5.6
V	3,4-Dimethyl- ^b	190	$C_{24}H_{20}O_2$	84.7	5.9	84.5	5.8
VI	4-Methoxy- ^c	177 ^d	$C_{23}H_{18}O_3$	80.7	5.3	80.9	5.2
VII	3,4-Dimethoxy- ^c	177 ^d	$C_{24}H_{20}O_4$	77.4	5.4	77.1	5.2
VIII	4-Chloro-	183	$C_{23}H_{16}O_2Cl$	76.1	4.3	76.2	4.4
IX	4-Chloro-3-methyl- ^c	189	$C_{24}H_{17}O_2Cl$	76.3	4.7	76.3	4.6
X	4-Bromo-	208	$C_{23}H_{17}O_2Br$	64.5	4.1	64.6	4.5

^a Prepared by the method of Adams and Noller, *THIS JOURNAL*, **46**, 1889 (1924).

^b This unsaturated compound may be isolated in a 15% yield when the commercial mixed dimethylacetophenones are condensed with benzil; it is interesting to note that it separates without traces of any other isomers.

^c Insol. in chloroform, and recrystallized from acetic acid, in which it is slightly soluble.

^d Mixed melting point, 148–150°.

^e For the preparation of this ketone and the 2-chloro-5-methyl isomer we are indebted to Mr. M. P. Bridgess.

The condensation is not brought about by the use of pyridine, piperidine, nor a trace of sodium methylate. Two g. of potassium hydroxide in 3 cc. of water and 25 cc. of methyl alcohol may be used, however, but the product is not of as good quality.

B. The Formation of the 4-Bromofuranes.—The unsaturated diketones readily form bromofuranes when solutions in glacial acetic acid or chloroform are treated with hydrogen bromide. The procedure is to dissolve 5 g. in 20 cc. of warm acetic acid and saturate the solution by

passing through a rapid current of dry hydrogen bromide gas. In some instances the bromofuranes separate almost immediately but always after standing overnight. They all form a white, bulky precipitate of needles that felt together on filtration, and show practically the same properties except melting point. Purification is best effected by dissolving in the minimum amount of hot chloroform and adding an equal volume of alcohol. The yields are practically quantitative.

TABLE II
2,3,5-TRIPHENYL-4-BROMOFURANE AND HOMOLOGS

No.	Group in position 5	M. p., °C.	Formula	Analyses			
				Calcd., C	% H	Found, C	% H
III	Phenyl ^a	129	C ₂₁ H ₁₅ OBr				
XI	4-Methyl-	134	C ₂₂ H ₁₇ OBr	71.0	4.4	70.8	4.5
XII	3,4-Dimethyl-	137	C ₂₄ H ₁₉ OBr	71.5	4.7	71.6	4.9
XIII	4-Methoxy-	151	C ₂₃ H ₁₇ O ₂ Br	68.1	4.2	67.9	4.2
XIV	4-Chloro- ^b	127	C ₂₂ H ₁₄ OCIBr	64.4	3.4	64.1	3.2
XV	4-Chloro-3-methyl-	135	C ₂₃ H ₁₆ OCIBr	65.4	3.8	65.4	3.9
XVI	4-Bromo- ^b	157	C ₂₂ H ₁₄ OBr ₂	58.1	3.1	58.0	3.1

^a This bromofurane has been prepared once previously by the action of heat on two stereoisomeric γ -bromo- γ -nitro ketones. E. P. Kohler, private communication.

^b Dissolved in 50 cc. of acetic acid.

The bromofuranes are very sparingly soluble in the alcohols, but dissolve readily in warm ether, chloroform, benzene and glacial acetic acid. They do not reduce permanganate in acetone solution nor decolorize bromine. The bromine atom is not affected by prolonged boiling with alkalis; bromide ion cannot be detected after twenty hours of heating with alcoholic potash. It does not react with magnesium to form a Grignard reagent, a result not unexpected, since the bromine atom is *di-ortho* substituted.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Benzil readily condenses with acetophenones substituted in the *meta* or *para* positions in the presence of an equivalent of sodium methylate to form derivatives of phenyldibenzoyl ethylene.

2. These substances react with hydrogen bromide in such a way that the product formed is a 4-bromofurane. The bromine atom in the latter substance is inactive.

TUFTS COLLEGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SILICON TETRACHLORIDE AS A REAGENT FOR THE PREPARATION OF ACID CHLORIDES^{1,2}

BY RALPH E. MONTONNA

RECEIVED JULY 13, 1927

PUBLISHED AUGUST 5, 1927

The action of silicon tetrachloride on organic acids has hitherto been but slightly investigated. Taurke³ obtained benzoyl chloride from benzoic acid by means of this reagent and Rauter⁴ prepared butyryl chloride by heating butyric acid with silicon tetrachloride in a sealed tube at 150–160°. These apparently constitute the only references in the literature.

In view of the author's previous success in the semi-industrial manufacture of acetyl chloride from acetic acid by this reagent (silicon tetrachloride), its action on other organic acids was investigated with a view to the preparation of a number of acid chlorides free from sulfur and phosphorus impurities.

The method followed was to dissolve the acid in an inert solvent (benzene, toluene, xylene, chloroform, etc.) and after raising the temperature to about 50° to run in the silicon tetrachloride. The acid chloride was distilled off through a fractionating column.

The mechanism of the reaction probably consists in the primary formation of a mixed anhydride of silicic and the organic acid,⁵ $4\text{RCOOH} + \text{SiCl}_4 = \text{Si(OCOR)}_4 + 4\text{HCl}$, and the secondary interaction of this with a further molecule of silicon tetrachloride, $\text{Si(OCOR)}_4 + \text{SiCl}_4 = 4\text{RCOCl} + 2\text{SiO}_2$. The following acids were investigated: acetic, propionic, butyric, isobutyric, benzoic, phenylacetic and sebacic, the yields obtained being 85, 50, 49, 51, 77, 61 and 37 per cent., respectively.

Other dibasic acids, *o*-nitrobenzoic and pyruvic acids were experimented with but negative results were obtained in all cases.

Experimental Part

Preparation of Acetyl Chloride.—Three hundred and sixty g. (six moles) of glacial acetic acid and 672 g. (six moles) of toluene are placed in a liter, round-bottomed, Pyrex flask fitted with a rubber stopper through which passed a dropping funnel and a reflux condenser. The upper portion of the latter is filled with glass beads and the condenser itself is, in turn, connected to an absorption system consisting of two wash-bottles containing acetic acid. The mixture is heated to 50° and at that temperature

¹ This paper is constructed from Part II of a dissertation presented by Ralph E. Montonna in June, 1924, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. The investigation was carried out in the laboratory of Dr. Harold Hibbert.

² Communicated to the Organic Division, American Chemical Society, Washington, D. C., April, 1924.

³ Taurke, *Ber.*, **38**, 1668 (1905).

⁴ Rauter, *Ann.*, **270**, 260 (1892).

⁵ Friedel and Ladenburg, *Ann.*, **145**, 174 (1868).

510 g. (three moles) of silicon tetrachloride is added from the dropping funnel during a period of 30 minutes. The same temperature is maintained until the vigorous evolution of hydrochloric acid almost ceases. The upright condenser is then replaced by a Glinsky or Hempel column carrying a thermometer and attached to a downward condenser, and the product fractionated over a free flame until the thermometer registers 80–85°. The product on redistillation gives 400 g. of acetyl chloride, b. p., 50–55°; yield, 85%.

The same method was applied to the other acids, the only difference being the use of other diluting media and a somewhat higher temperature, prior to fractionation, to ensure the completeness of the reaction.

The results obtained are tabulated below.

TABLE I
SUMMARY OF RESULTS

Exp. no.	Acid used,		Solvent	g.	SiCl ₄ , g.	Temp., °C.	Acid chloride recovered		
	name	amt., g.					g.	%	b. p., °C.
1	Propionic	148	Xylene	212	170	50	93	50	75–80
2	Butyric	176	Xylene	212	170	50	104	49	102–105
3	Isobutyric	176	Xylene	212	170	50	109	51	93–98
4	Isobutyric	88	Xylene	106	85	50	56	52.5	93–98
5	Benzoic	122	None	...	85	50	32	23	192–195
6	Benzoic	122	Benzene	135	90	50	108	77	194–196
7	Phenylacetic	272	Benzene	186	170	60	Decomp. on distillation		
8	Phenylacetic	136	Benzene	120	85	60	94	61	115–125/30 mm.
9	Sebacic	50.5	Benzene and ether	175	42.5	50	22	37	185–195/30 mm.
10	Maleic	58	Benzene and ether	175	42.5	50	None		
11	Malonic	52	Benzene and ether	195	85	50	None		
12	Malonic	52	Xylene	106	85	100	None		
13	Oxalic	90	Ether	100	170	50	None		
14	Oxalic	90	Ether and benzene	240	170	75	None		
15	Oxalic	90	Ether	100	170	0	None		
16	o-Nitrobenzoic	42	Benzene	80	22	50	None		
17	o-Nitrobenzoic	42	Ether	75	22	50	Blew up on distill.		
18	o-Nitrobenzoic	42	Ether and benzene	160	22	50	Crude product only		
19	Pyruvic	88	Chloroform	120	90	50	None		
20	Pyruvic	50	Ether	100	50	–10	None		

Synthesis of Acetic Anhydride

The same reagent (silicon tetrachloride) can also be used for the preparation of acid anhydrides from the sodium salts of the corresponding acid using a diluent, preferably the anhydride itself.

In the following experiment acetic anhydride itself was used as diluent. 130 g. of anhydrous sodium acetate and 300 g. of 99% acetic anhydride were warmed to 50° and, while stirring, 67 g. of silicon tetrachloride was added during a period of one hour. The temperature rose to 80° and the heating was continued for three hours at 90°. The yield was 75% of 96% anhydride.

A second experiment carried out in glassware, using benzene as diluent and heating for five hours at 50–60°, gave a yield of 50%.

Summary

A laboratory method is described for the preparation of "phosphorus-

This is a difficult task. The quantum theory still contains so many uncertainties that a convincing elementary exposition is not yet possible, and one hundred pages is too short for any serious contribution to the extensive field that the author covers. The book, however, fulfils the author's own intention of giving a rapid survey of the whole field and contains references to a very considerable number of original contributions.

RICHARD C. TOLMAN

Die Verwendung der Röntgenstrahlen in Chemie und Technik. Ein Hilfsbuch für Chemiker und Ingenieure. (The Application of X-rays in Chemistry and Technology. A Reference Book for Chemists and Engineers.) By Dr. HERMANN MARK. Johann Ambrosius Barth, Salomonstrasse 18B, Leipzig, Germany, 1926. xv + 528 pp. 328 figs. 25.5×18 cm. Price, unbound, Rm. 48; bound, Rm. 50.

Among a list of great books already published on the various ramifications of x-ray science, there always seems to be a place for a new contribution, particularly if it emphasizes the new practical applications of a fundamental research tool. No one is better qualified by training, experience and personality to prepare a great treatise than Dr. Mark. His x-ray experiments have ranged from the purest physics to the most practical (but always thoroughly scientific) studies of the structure of rubber, worked metals and engineering materials; he assisted Polanyi in working out the complete interpretation of fiber structures which play so important a part in natural and manufactured materials.

The book is really magnificently painstaking, authoritative and complete. The advances which have been made in so few years since crystals were found to serve as diffraction gratings for x-rays are most picturesquely set forth by a comparison of the content of this encyclopedic book with the first edition of the pioneer book on x-rays and crystal structure by the Braggs, published scarcely more than a decade ago. The observer has the same feeling that he has in comparing side by side a modern, mountain-climbing super-locomotive with a courageous little "Dewitt Clinton."

The title of Dr. Mark's book is somewhat of a misnomer. The applications of x-rays in chemistry and industry are not set forth as present achievements and future possibilities so that an executive or research director might learn whether or not he had an x-ray problem. There is nothing which may be classed as introductory, popular or missionary about this contribution. It is distinctly a methodology, and as such leaves nothing to be desired, for it is doubtful if more solid "meat" was ever crammed into 528 pages.

The first section on the production of x-rays is certainly the most detailed and complete exposition of high-tension apparatus and x-ray tubes to be found anywhere. In some respects this is the best and most

original part of the book. The second section on the spectroscopy of x-rays shows the strong influence of Siegbahn's book, as is to be expected for this subject. The third section on crystal structure analysis with the help of x-rays follows the scheme of presentation in Ewald's great book, but of course goes far beyond upon the basis of recent developments. Mark's presentation of crystal symmetry, space groups and interpretation is the most logical and complete thus far published, although a chemist or engineer untrained in the subject would make difficult progress through the material. The fourth section on the determination of crystal grain orientation and particle size is disappointing in that it is not as thoroughly complete as might be hoped from an experimenter who has had a large hand in the development of these subjects. It will still be necessary to consult the series of original papers by Polanyi, Mark and others on fibering and deformation, for information as to mathematical interpretation. The last section on literature references and notes is interesting and valuable for those engaged in research.

The student (he must be this, rather than a reader) will often have the wish that more actual examples of analysis and application were given. This would, of course, prolong a book already voluminous, but it might have been done very advantageously at the expense of some of the spectroscopic data easily available elsewhere. The fact remains, however, that as a thorough handbook of experimental and interpretational methods to be used by relatively well-trained scientists, Dr. Mark's work has no equal, and if later editions keep the subject matter up to date (at the present rate of discovery a revision will certainly be required every year) it may well continue to dominate in the training of those who attempt to apply x-rays to problems of chemistry and industry.

GEORGE L. CLARK

Forschungen zur Kristallkunde: I. Trachten der Kristalle. (Researches in the Science of Crystals: I. The Habit of Crystals.) By H. TERTSCH, University of Vienna. Bornträger, Berlin, 1926. viii + 222 pp. 58 figs. 17 × 25 cm. Price 15 M.

This is the first of a new series of monographs on crystallography and related subjects, under the editorship of Professor Arrien Johnsen, of the University of Berlin. It comprises chapters on the domain of the work, methods of measurement, observations on influencing habit, the habit significance of forms, peculiarities of surface development, and the theory of the subject. There is a bibliography of 181 titles, practically all of German articles, although in some way two or three references to American journals have managed to creep in, and 12 papers by Gaubert in French are included.

Bringing together as it does material widely scattered through the

literature, this book serves a useful purpose. Chemists will be especially interested in the discussion of influencing habit by physical and chemical means, and in the theoretical treatment on the basis of the space-lattice arrangement of atoms or molecules in crystals.

EDGAR T. WHERRY

Die Herstellung kolloider Lösungen anorganischer Stoffe. (The Preparation of Colloidal Solutions of Inorganic Substances.) By Dr. JOSEF REITSTÖTTER. Theodor Steinkopff, Dresden and Leipzig, 1927. 62 pp. 2 figs. 25.5 × 18 cm. Price, unbound, M. 3.

The first fourteen pages are devoted to a brief discussion of methods of forming colloidal solutions, and the function of protective colloids. The methods are classified according to Svedberg's classification into dispersion and condensation methods. The rest of the book enumerates the methods which have been used to make colloidal solutions of various inorganic substances. The arrangement followed is to discuss each element and its most important compounds in the order of its occurrence in the periodic table rather than grouping together similar methods of preparation for different substances. This arrangement, the numerous references to scientific and patent literature and the adequate indexes make it convenient and valuable as a reference book.

NORMAN D SCOTT

A Handbook of Organic Analysis. Qualitative and Quantitative. By HANS THACHER CLARKE, D.Sc., F.I.C., with an introduction by J. NORMAN COLLIE, Professor of Chemistry in University College, London. Fourth edition. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1926. xii + 363 pp. 23 figs. 19 × 12.5 cm. Price \$3.00.

The first edition of this excellent book appeared fifteen years ago, the present edition being the fourth. An extensive revision has been necessary owing to the progress made in the meantime in organic chemistry.

The first chapter deals with such topics as purity, general characteristics, methods for examination for the elements, determination of the approximate constitution and a tabular summary of preliminary tests. The second takes up the examination for various radicals and this is followed by a chapter on the separation of mixtures. Chapter IV (287 pages) gives classified tables of organic compounds, the members of each group being arranged according to melting point or boiling point. The characteristic behavior of each substance is indicated, that is, reactions particularly useful in identification.

Chapter V describes quantitative methods for the most important elements, followed by a chapter on the quantitative determination of certain radicals. The last chapter describes the methods for determining molecular weight, vapor density, density of liquids and optical rotation.

I believe a more thorough-going dependence on solubility relations would give a better system of analysis. I would also considerably abbreviate the section of compounds and their behavior so as to compel the student to rely more on the library. Quantitative methods might be left out entirely as we have satisfactory descriptions in organic laboratory manuals. As this is a book for beginners in analysis, it should be reduced to the smallest size possible.

ALVIN S. WHEELER

The Preparation and Analysis of Organic Compounds. By J. BERNARD COLEMAN and FRANCIS ARNALL. P. Blakiston's Son and Company, 1012 Walnut Street, Philadelphia, 1926. xvi + 352 pp. 42 figs. 22.5 × 14.5 cm. Price, \$4.00.

In 352 pages the authors have succeeded in presenting the important fields of organic chemistry laboratory work. This is done in five sections and an appendix. I. General processes dealing with the purification of compounds and the determination of physical constants. II. Directions for the preparation of 89 individual compounds arranged according to types of compounds prepared. The directions are preceded by brief statements of the theory and by the chemical equations involved. III. Qualitative analysis. The scheme involves grouping compounds in classes according to their elementary composition. The method, although much less extensive, has many points of resemblance to that of Mulliken, particularly noticeable in the group containing carbon and hydrogen (and oxygen). It is difficult to determine without actual trial if this scheme will in general take less time than the Mulliken procedure and if so whether or not this will outweigh the greater precision of the latter. IV. Ultimate analysis. V. Determination of molecular weights and the estimation of typical groups.

The book is well worth looking over, particularly by those who wish to have a limited treatment of the fields of organic laboratory work included under one cover. In general, the experiments are well chosen but the description of apparatus, particularly in the section on quantitative analysis, is in a few cases not strictly modern.

R. R. RENSHAW

Organische Molekülverbindungen. (Organic Molecular Compounds.) Second, revised edition. By Dr. PAUL PREIFFER, Professor of Chemistry at the University of Bonn. Ferdinand Enke, Stuttgart, 1927. xvii + 470 pp. 4 figs. 16.5 × 25.5 cm. Price, unbound, M. 40; bound, M. 42.20.

This edition, though considerably enlarged, follows closely the lines of the first edition. There is an introductory section setting forth the Werner coördination theory, first as applied to inorganic and then to organic molecular compounds. The second section discusses at length mixed inorganic-organic molecular compounds, classified primarily according to the inor-

ganic element whose residual affinity is involved. The third section presents the purely organic molecular compounds. There are two new chapters in this section: one on the detection, preparation and properties of purely organic molecular compounds, and another on the significance of these compounds in the theories of adsorption, solution and crystal structure. The fourth and last section discusses the mechanism of chemical reactions on the basis of molecular compounds as intermediate steps.

This book is on the one hand a valuable systematic compilation of organic molecular compounds, previously for the most part widely scattered through the voluminous literature of organic chemistry, and on the other an instructive discussion of their theoretical relationships.

ARTHUR B. LAMB

Practical Organic and Bio-Chemistry. By R. H. A. PLIMMER, D.Sc., Professor of Chemistry in the University of London. New Edition. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1926. x + 568 pp. 67 figs. 25.5 × 16 cm. Price \$7.50.

In the course of several editions this work, "originally compiled as a handbook of practical work for medical students," has been enlarged to serve "as a textbook and practical book" on organic chemistry, and in this revision "additional matter has been added to the section on physiological chemistry." The formidable task of condensing the essentials of what are usually regarded as two fields of science into less than 550 pages has been accomplished by virtue of a logical arrangement of material, the detailed discussion of only those portions of organic chemistry of interest to physicians, and a clear and concise style. The direct, positive statements which serve well in the exposition of the established facts and classifications of organic chemistry are not, however, suited to the discussion of some of the newer and more controversial topics treated in the physiological section, where detailed evidence and a critical attitude are demanded. For example: "Shortage of vitamin C is associated with a sallow, muddy complexion and pseudo-rheumatic pains." (p. 507.)

The book is unusual among biochemical texts in that the symbol *PH* appears but once, and then without explanation. In general, the contributions of physical chemistry to biochemistry are given but slight attention, and the discussion of the blood as a carrier of gases is consequently inadequate. There is a chapter of seventeen pages on colloids and colloidal solutions.

The presence of the formulas of Harrington for thyroxin, and of Stewart and Tunncliffe for glutathione indicates that the present edition contains much recent material on the organic side of the subject. The directions for practical work are embodied in direct statements of fact rather than in questions to be answered by experiment.

F. F. HEYROTH

Lehrbuch der Enzyme. Chemie, Physikalische Chemie, und Biologie. (Textbook of Enzymes. Chemistry, Physical Chemistry and Biology.) By Professor CARL OPPENHEIMER with Dr. RICHARD KUHN. Georg Thieme, Leipzig, 1927. iv + 660 pp. 18 figs. 25 × 17 cm. Price, unbound, RM 33; bound, RM 36.

This is offered by the authors and publisher both as an essentially new book and as a fifth and completely rewritten edition of Oppenheimer's well-known textbook on enzymes. The main divisions of the book are: I, General chemistry of enzymes, 150 pages; II, Biology of enzymes, 54 pages; III, The hydrolases, 250 pages; IV, The desmolases, 195 pages. Of these, Sections I and II constitute the "general," and III and IV the "special" parts. Section I includes general introductory matter, the classification of enzymes, their descriptive chemistry, the influence of various factors upon enzymic activity, its physical chemistry and kinetics; Section II, the occurrence and formation of enzymes in nature and their significance in the economy of the living organism; Section III describes the esterases, carbohydrases, nucleases, amidases and proteases; Section IV, the general conceptions of oxidation-reduction enzymes, the zymases, dehydrases and catalases.

Notwithstanding the size and scope of this book, much of it gives the impression of expression of the authors' views rather than of mere compilation; but it can hardly be said that these views appear always to have been formed from an even weighing of all the evidence. The authors have evidently given much more attention to the original work which has been published in the German language than to that which has been published in English.

The book is written in the style in which one addresses advanced readers, the names of investigators appearing freely in the text, but in most cases the references to original papers are unfortunately not given, so that the book, while comprehensive and suggestive, does not serve effectively to put the reader in touch with all the more important of the original literature.

It would seem that this paucity of references must detract rather seriously from the value of a book of this size to many of its readers, but to those who are already accustomed to following the original literature of the enzymes this work will be of interest for its suggestiveness and as a summary of the views of its authors. It seems unfortunate that these writers should adopt so dogmatically and emphasize so often the view that Willstätter's purified enzyme preparations contained neither protein nor carbohydrate, when a study of the actual experimental evidence of Willstätter's and other investigations bearing upon the question would have shown them that no such general negative is proved. The authors' views upon the recent physical chemistry of the enzymes are well summarized in this work.

H. C. SHERMAN

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID IV. AMMONIUM AND TETRAMETHYLAMMONIUM AZIDO-DITHIOCARBONATES; TETRAMETHYLAMMONIUM THIOCYANATE^{1,2}

BY L. F. AUDRIETH, G. B. L. SMITH AND A. W. BROWNE

WITH MICROSCOPICAL STUDIES BY C. W. MASON

RECEIVED DECEMBER 23, 1926

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In view of the peculiar photosensitivity of the rubidium and cesium azido-dithiocarbonates,^{1c} it has been thought probable that the tetramethylammonium salt might, like these compounds, show a reversible color change under the influence of light. The chief objective of the present investigation has therefore been the isolation and description of this substance, which should be of interest in any event from the fact that it contains a strongly electropositive radical, or "synthetic metal" in combination with a strongly electronegative radical of the halogenoid type. For the sake of comparison, the hitherto unknown ammonium azido-dithiocarbonate has also been prepared, as well as the tetramethylammonium thiocyanate, the principal product of the thermal decomposition of tetramethylammonium azido-dithiocarbonate.

¹ For the earlier articles of this series see (a) Smith and Wilcoxon with Browne, *THIS JOURNAL*, **45**, 2604 (1923); (b) Browne and Smith, *ibid.*, **47**, 2698 (1925); (c) Browne and Audrieth, *ibid.*, **49**, 917 (1927).

² The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article 3 under Heckscher Grant No. 60. For Articles 1 and 2, see (a) *THIS JOURNAL*, **45**, 2604 (1923); (b) **47**, 1916 (1925). For articles 1, 2, 3 and 4 under Heckscher Grant No. 4, see (c) *ibid.*, **44**, 2106 (1922); (d) **44**, 2116 (1922); (e) **44**, 2315 (1922); (f) **45**, 2541 (1923).

Ammonium Azido-dithiocarbonate³

This compound may be obtained (1) by neutralization of free azido-dithiocarb acid^{1a} with ammonium hydroxide in aqueous solution, (2) by prolonged treatment of ammonium trinitride in aqueous solution with carbon disulfide under conditions prescribed for use in the synthesis of the potassium salt,^{2b} and (3) by bubbling ammonia gas through an ethereal solution of the azido-acid. The third procedure, which is similar to the method used by Browne and Houlehan⁴ in preparing ammonium trinitride, was adjudged the most satisfactory for the present investigation.

The ammonium radical was determined in the usual way after distillation of the ammonia from alkaline solution into standard sulfuric acid. The azido-dithiocarbonate radical was determined by the modified Volhard method recommended by Browne and Smith.^{1b}

Anal. (a) Subs., 0.6584, 0.7965: NH_4 , 0.0864, 0.1063. Calcd. for NH_4SCSN_3 : NH_4 , 13.25. Found: 13.12, 13.35. (b) Subs., 0.3097, 0.1783: SCSN_3 , 0.2694, 0.1505. Calcd. for NH_4SCSN_3 : SCSN_3 , 86.8. Found: 87.0, 86.8.

Ammonium azido-dithiocarbonate is a white, crystalline, non-deliquescent solid, readily soluble in water, methyl or ethyl alcohol, and acetone, somewhat soluble in ether, but practically insoluble in benzene and xylene.

Heated in a Thiele melting-point tube the ammonium salt assumes at 90° a reddish-orange color, RO-O on the Milton Bradley Standard.⁵ Decomposition becomes perceptible at about 110°, and the substance melts with evolution of gas at about 120°. The residue was found to consist of ammonium thiocyanate and sulfur, indicating that the reaction proceeds in accordance with the equation $\text{NH}_4\text{SCSN}_3 = \text{NH}_4\text{SCN} + \text{S} + \text{N}_2$. Larger samples have been found to decompose suddenly, with a puff, between 115 and 120°.

Samples composed of larger crystals obtained by the second method were invariably found to decrepitate vigorously between 80 and 100° as a result of the presence of occluded nitrogen formed during prior thermal decomposition. When such crystals are dissolved in water the presence of these occluded gases becomes manifest.

On exposure to direct sunlight the salt undergoes coloration, within a few minutes, to a very light orange tint, OT2 on the Milton Bradley Standard.⁵ A partial reversal of this color change takes place very slowly in the dark.

When strongly heated on an asbestos board, the salt suddenly decomposes with considerable flame and a puff of smoke. An attempt to effect a molecular rearrangement of the salt by heating a sample in a sealed tube resulted in a violent explosion.

Under the microscope, ammonium azido-dithiocarbonate is seen to form crystals that are mostly thick, six-sided tablets of varying proportions. The parallel or symmetrical extinction exhibited in more than one position, together with the crystal forms present, indicate that the substance very probably is orthorhombic. The terminal angle of the truncated rhomb-shaped crystals is about 120°. Numerous forms are represented on well-developed crystals: 001, 100, 010, 111, 211, 110, and probably other forms as well, may be recognized. The index of refraction is about 1.9 for vibrations

³ The authors would express, herewith, their appreciation of the assistance rendered by Mr. G. G. Parker, of this Laboratory, in connection with a part of the experimental work upon this substance.

⁴ Browne and Houlehan, *THIS JOURNAL*, 33, 1742 (1911).

⁵ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1st ed., 1905, Vol. I, p. 232.

parallel, and 1.7+ for vibrations perpendicular, to the long diagonal of the rhomb-shaped forms. Double refraction is strong; the interference figure is biaxial, but the axial angle is so large that the acute bisectrix and the sign of double refraction cannot be determined with certainty. The axial plane is parallel to the short diagonal of the rhomb-shaped forms.

Tetramethylammonium Azido-dithiocarbonate $N(CH_3)_4SCSN_3$

Three methods for the preparation of this substance have been studied: (1) neutralization of free azido-dithiocarbonic acid with tetramethylammonium hydroxide in aqueous solution, (2) double decomposition of barium azido-dithiocarbonate and tetramethylammonium sulfate, and (3) digestion of an aqueous solution of tetramethylammonium trinitride, a compound first prepared in this Laboratory by Friedlander,⁶ with an amount of carbon disulfide slightly in excess of that required by the equation $N(CH_3)_4N_3 + CS_2 = N(CH_3)_4SCSN_3$. The third method, carried out under the conditions specified by Browne and Hoel,²⁰ was found most satisfactory for use in the current investigation.

Nitrogen was determined by the Dumas method, and the azido-dithiocarbonate radical by the modified Volhard procedure.^{1b}

Anal. (a) Subs., 0.1164, 0.1054: N_2 (corr.), 26.9, 24.2 cc. Calcd. for $N(CH_3)_4SCSN_3$: N_2 , 29.1. Found: 28.9, 28.7. (b) Subs., 0.2217, 0.2220: $SCSN_3$, 0.1362, 0.1360. Calcd. for $N(CH_3)_4SCSN_3$: $SCSN_3$, 61.5. Found: 61.4, 61.3.

The tetramethylammonium salt crystallizes from aqueous solution in the form of large, white tablets, which may be purified by recrystallization from warm alcohol. The addition of ether to an alcoholic solution results in the precipitation of the salt in a voluminous, finely divided mass. The compound is readily soluble in water, fairly soluble in either methyl alcohol or acetone, slightly soluble in ether, and insoluble in carbon tetrachloride, carbon disulfide and chloroform.

The salt does not explode when struck with a hammer. When thrown upon the hot plate, or heated directly in the Bunsen flame, it suddenly decomposes with a puff. Heated gently, the substance always yields the characteristic odor of trimethylamine, which indicates that the primary decomposition of the substance may involve its dissociation into the tertiary amine and methyl azido-dithiocarbonate, in accordance with the equation $N(CH_3)_4SCSN_3 = N(CH_3)_3 + CH_3SCSN_3$.

In the melting-point tube the substance apparently undergoes fusion at 95–98°, assuming at the same time a dark green color. The color change is usually followed by a sudden puff indicative of complete decomposition. Like all other azido-dithiocarbonates thus far studied the tetramethylammonium salt gradually decomposes, even at room temperature, with formation of the thiocyanate, sulfur and nitrogen. In aqueous solution the negative ion resists decomposition for a time, and only after several hours of vigorous boiling fails to respond to the usual qualitative tests.

On exposure at room temperature to direct sunlight the white salt in a few minutes assumes a light orange color, OT1 on the Milton Bradley Standard.⁵ In the dark this effect undergoes a gradual reversal which takes place more slowly than in the case of the cesium salt.¹⁶ Further work on the photosensitivity of the tetramethylammonium salt and of various other azido-dithiocarbonates and related compounds is now in progress.

Under the microscope the salt is seen to crystallize from aqueous solution in the form of rectangular tablets and stout prisms with beveled long edges. Some crystals show parallel extinction and give biaxial interference figures. They are optically positive, with 2V rather small, the axial plane being parallel to the elongation of the tablets, and

⁶ Friedlander, *THIS JOURNAL*, 40, 1945 (1918).

the acute bisectrix perpendicular to their principal plane. Other crystals, lying on one of the beveling faces, give oblique dispersed extinction and somewhat anomalous polarization colors. The maximum extinction angle observed is about 40° for the position corresponding to an edge view of the elongated tablets. Some end views were observed and these showed parallel extinction. The optical properties and symmetry of the crystals point to their being in the monoclinic system.

Tetramethylammonium Thiocyanate $N(CH_3)_4SCN$

In connection with a study of the power of solution and ionization of various non-aqueous solvents towards binary salts, Walden⁷ prepared tetramethylammonium thiocyanate (1) by heating methyl thiocyanate with a solution of trimethylamine. During the current research this method has been compared with two others, by which the salt is obtainable either (2) by prolonged boiling of an aqueous solution of tetramethylammonium azido-dithiocarbonate, until quantitative decomposition into the thiocyanate has occurred, or (3) by bringing together tetramethylammonium trinitride⁸ and carbon disulfide in alcoholic solution and boiling under the reflux condenser until the reaction has proceeded to completion.⁸ The third method was found most convenient. Four cc. of carbon disulfide was dissolved in 50 cc. of absolute alcohol, and 5 g. of tetramethylammonium trinitride was added little by little to the boiling solution, which was refluxed until qualitative tests indicated the absence of trinitrides and azido-dithiocarbonates. After the solution had been concentrated and cooled, the thiocyanate was recrystallized from alcohol and obtained in the form of glistening white needles.

Nitrogen was determined by the Dumas method, and thiocyanogen was weighed as the silver salt.

Anal. (a) Subs., 0.1654, 0.1787: N_2 (corr.), 28.23, 30.45 cc. Calcd. for $N(CH_3)_4SCN$, N_2 , 21.2. Found: 21.35, 21.32. (b) Subs., 0.1933, 0.1847: $AgSCN$, 0.2413, 0.2310. Calcd. for $N(CH_3)_4SCN$: SCN , 43.9. Found: 43.7, 43.8.

Tetramethylammonium thiocyanate is fairly soluble in water and methyl alcohol, slightly soluble in ethyl alcohol and acetone, and insoluble in ether, chloroform, carbon disulfide and carbon tetrachloride.

When heated in the melting-point tube, the substance volatilizes at $304\text{--}305^\circ$. From the odor it is apparent that thermal dissociation into the tertiary amine and methyl thiocyanate readily takes place. By dry distillation a yellowish oil which boils at 132° (b. p. of CH_3SCN , 133°) is obtained.

Under the microscope the salt crystallizes in rectangular prisms with the long edges beveled, and in tabular crystals (flattened prisms). A few end views were obtainable, and these corresponded to the prismatic forms in symmetry and optical properties. The crystals exhibit parallel extinction in all positions, with moderately strong birefringence. They are biaxial, optically positive, with $2V$ rather small. The plane of the optic axis is parallel to the elongation of the tabular forms, and the acute bisectrix is perpendicular to their principal plane. The symmetry and optical properties indicate that the crystals are in the orthorhombic system.

Tetramethylammonium thiocyanate is empirically isomeric, not only with tetramethyl thio-urea,⁹ but also with numerous other derivatives

⁷ Walden, *Z. Elektrochem.*, **27**, 34 (1921).

⁸ Stollé [*Ber.*, **55**, 1289 (1922)] has shown that sodium trinitride and carbon disulfide react in boiling alcoholic solution to form sodium thiocyanate, free sulfur and nitrogen gas. The fact that sodium azido-dithiocarbonate was undoubtedly formed as an intermediate product seems to have escaped the notice of this investigator.

⁹ Billeter, *Ber.*, **43**, 1853 (1910).

of thio-urea, including the *sym.*-diethyl,¹⁰ *isobutyl*,¹¹ *sym.*-butyl,¹² normal butyl,¹³ *d-sym.*-butyl,¹³ methyl *sym.*-propyl,¹⁴ α, α' -dimethyl- β -ethyl,¹⁵ and *unsym.*-diethyl¹⁶ thio-ureas. In the thought that the tetramethylammonium salt might undergo transformation into tetramethyl thio-urea, several preliminary experiments have been performed. No evidence of such a molecular rearrangement has thus far been obtained.

Summary

Two new compounds, ammonium azido-dithiocarbonate, NH_4SCSN_3 , and tetramethylammonium azido-dithiocarbonate, $\text{N}(\text{CH}_3)_4\text{SCSN}_3$, have been prepared and described. Both are white, crystalline solids, fairly stable at room temperature, but decomposing rapidly, and under certain conditions explosively, when heated. Both undergo a curious color change; the former when either heated or illuminated, the latter when illuminated at ordinary temperature.

Tetramethylammonium thiocyanate, a product of the thermal decomposition of the tetramethylammonium azido salt, has also been prepared and studied.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE VOLUMETRIC DETERMINATION OF HYDRAZOIC ACID BY OXIDATION WITH CERIC SULFATE IN ACID SOLUTION

By JEROME MARTIN

RECEIVED MARCH 3, 1927

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Sommer and Pincas¹ developed a nitrometric method for determining hydrazoic acid which depends on its oxidation by a ceric salt in acid solution, and showed that the nitrogen evolved corresponds to the reaction $2\text{Ce}^{++++} + 2\text{HN}_3 = 3\text{N}_2 + 2\text{Ce}^{+++} + 2\text{H}^+$. In the present investigation an iodimetric method based on this reaction has been found to give satisfactory results. A measured quantity of a stock solution of ceric sulfate is added and the excess is determined iodimetrically. The writer is not aware of any other titration method which depends on the oxidation of hydrazoic acid.²

¹⁰ Hofmann, *Ber.*, 1, 25 (1868).

¹¹ Hofmann and Reimer, *Ber.*, 3, 755 (1870).

¹² Hofmann, *Ber.*, 7, 508 (1874).

¹³ Urban, *Arch. Pharm.*, 242, 51 (1904), through *Chem. Zentr.*, 1904, I, 997.

¹⁴ Hecht, *Ber.*, 23, 281 (1890).

¹⁵ Billeter and von Pury, *Ber.*, 26, 1681 (1893).

¹⁶ Wallach, *Ber.*, 32, 1872 (1899).

¹ Sommer and Pincas, *Ber.*, 48, 1963 (1915).

² The volumetric method of West, *J. Chem. Soc.*, 77, 705 (1900). Riegger [THIS JOURNAL, 33, 1569 (1911)] depends on the distillation of hydrazoic acid and its titration with standard alkali.

Preparation of Solutions

The hydrazoic acid used in this work was prepared by the method of Browne.³ From this a stock solution of sodium azide was made by neutralization with sodium hydroxide. This stock solution was standardized by the gravimetric method of Turrentine and Olin,⁴ and the average value of five determinations was $0.1097 \pm 0.1\%$.

Two different stock solutions of ceric sulfate were prepared and standardized iodimetrically.⁵ Solution A was prepared by the electrolysis of cerous sulfate in 6 *N* sulfuric acid. Solution B was obtained by diluting with water a paste of ceric oxide and concd. sulfuric acid until the acid concentration was 2 *N*. The latter method is preferable since it is easier to carry out.

The thiosulfate solution was standardized against known potassium permanganate solution⁶ which had been standardized against Bureau of Standards sodium oxalate.

The Standard Procedure is as follows. The air in a ground-glass stoppered flask is displaced by a current of nitrogen or carbon dioxide, and the neutral or slightly basic solution of hydrazoic acid added. A

TABLE I

DETERMINATION OF 0.1097 <i>M</i> HYDRAZOIC ACID WITH CERIC SULFATE								
Expt.	Ceric sulfate soln. used	NaN ₃ taken, cc.	Final volume, cc.	Approx. concn. of acid, <i>N</i>	Time, in min.	Vol. of thio. calcd. as 0.1 <i>N</i>	Vol. of Ce ⁺⁺⁺ calcd. as 0.1 <i>M</i>	Calcd. concn. of NaN ₃
1	A	9.982	300	0.3	5	10.60	21.57	0.1099 ^a
2	A	9.982	300	.3	5	10.62	21.57	.1097 ^a
3	A	9.982	300	.3	5	10.60	21.57	.1099 ^a
4	A	9.982	500	.2	5	32.16	43.14	.1100 ^a
5	B	25.06	500	.12	5	0.84	28.33	.1097
6	B	25.06	500	.12	5	.87	28.33	.1096
7	B	25.06	500	.12	5	.85	28.33	.1097
8	B	25.06	500	.12	10	.87	28.33	.1096
9	B	25.06	500	.12	15	.85	28.33	.1097
10	B	25.06	500	.12	1	.95	28.33	.1092 ^a
11	B	25.06	500	.12	1	.98	28.33	.1091 ^a
12	B	25.06	500	.20	5	12.95	40.41	.1096
13	B	25.06	500	.20	5	12.93	40.41	.1097
14	B	25.06	500	.20	1	12.98	40.41	.1095 ^a
15	B	25.06	500	{ .12H ⁺ .2M NH ₄ ⁺ }	5	0.87	28.33	.1096
16	B	25.06	500		5	.85	28.33	.1097

Av. 0.10965 \pm 0.1%

^a These values were not used in computing the average.

³ Browne, *THIS JOURNAL*, **27**, 551 (1905).

⁴ Turrentine and Olin, *ibid.*, **37**, 1118 (1915).

⁵ Brauner, *Z. anorg. Chem.*, **34**, 207 (1903).

⁶ Bray and Miller, *THIS JOURNAL*, **46**, 2204 (1924).

measured excess of a standard ceric sulfate solution is quickly added, the flask stoppered, shaken vigorously, and allowed to stand for five minutes. An excess of potassium iodide is then added and the liberated iodine titrated with 0.1 *N* thiosulfate solution, using starch as an indicator. A solution of 0.01 *N* iodine may be used to determine the end-point more exactly.

The experimental results are shown in Table I.

Discussion of Experimental Results

Expts. 1-4 in which Solution A was used cannot be given much weight since the high acid concentration would accentuate the oxygen error, due to a trace of residual oxygen, either in the standard procedure or in the standardization of the stock ceric sulfate solution.

The reaction is complete in five minutes under the conditions employed, but Expts. 10, 11 and 14 show that it is not complete in one minute.

That the excess of ceric salt does not affect the results is shown by comparing Expts. 12-13 with Expts. 5-9. This indicates that the reaction is smooth, and free from side reactions.

That ammonium ion has no effect on the ceric ion-hydrazoic acid reaction is shown by Expts. 15 and 16 which differed from the standard procedure only in that 5 g. of ammonium sulfate was dissolved in the solution of sodium azide before the ceric sulfate was added. Additional experiments showed that ammonium ion is slowly oxidized at boiling temperature when the acid concentration is high (about 20 *N*), but not under other conditions.

The method cannot be used in the presence of hydrazine since it is oxidized rapidly by ceric salt, the products being nitrogen and ammonium ion. More nitrogen is evolved than corresponds to the equation,⁷ $2\text{Ce}^{++++} + 2\text{N}_2\text{H}_4 = \text{N}_2 + 2\text{NH}_4^+ + 2\text{Ce}^{+++} + 2\text{H}^+$. However, the hydrazoic acid can be distilled from the acid solution of hydrazine.

The two sources of error are the volatility of the hydrazoic acid in acid solution, and the catalytic effect which cerous ion exerts on the oxygen-iodide reaction. When the acid concentration is low, the latter error may be rendered negligible by using oxygen-free water and sweeping out the reaction flask with nitrogen. The effect of the volatility of the hydrazoic acid was reduced by adding the ceric sulfate quickly, stoppering the flask and shaking vigorously.

The author wishes to thank Professor William C. Bray for his suggestions and interest in this work.

Summary

Hydrazoic acid has been determined volumetrically by a method which depends upon the oxidation of hydrazoic acid to nitrogen by ceric sulfate

⁷ Benrath and Ruland, *Z. anorg. Chem.*, 114, 287 (1920).

in acid solution. The method is accurate to within 0.1% if care is taken to eliminate the oxygen-iodide error and if the loss of hydrazoic acid by volatilization is prevented. Hydrazoic acid cannot be determined in the presence of hydrazine, but the two can be readily separated. Ammonium ion has no effect on the method.

BERKELEY, CALIFORNIA

[CONTRIBUTION NO. 36 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE ADSORPTION OF HYDROGEN AND ETHYLENE ON A COPPER CATALYST POISONED WITH CARBON MONOXIDE

BY CARROLL W. GRIFFIN

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Some years ago Taylor and Burns¹ in studying the adsorption of gases on metallic catalysts found that catalytically active copper adsorbed ethylene strongly at low temperatures and hydrogen less strongly. Later Pease² took up the study of the hydrogenation of ethylene using copper as the catalyst. He pointed out the apparent correlation of catalytic activity and strong or low-pressure adsorption of reactants in view of the fact that either mercury poisoning or heat treatment of the copper caused a simultaneous and marked decrease of both of these properties. This was followed by a study by Pease and Stewart³ of the effect of carbon monoxide as a poison to the reaction. They showed that less than 0.05 cc. of carbon monoxide reduced by 88% the activity (towards an ethylene-hydrogen mixture) of a copper catalyst which adsorbed at less than one mm. pressure approximately 1 cc. of hydrogen, 2 cc. of ethylene or 5 cc. of carbon monoxide. Their conclusion was that the copper surface owed 88% of its catalytic activity to less than 1% of the centers active in adsorption, thus emphasizing the existence on the copper surface of centers of different degrees of activity. The adsorption of the reactants on the catalyst poisoned with carbon monoxide had not been measured and it was suggested to the writer by Dr. R. N. Pease that such measurements be made.

Procedure

The apparatus, the method of preparation of the catalyst, of the hydrogen and of the ethylene, as well as the taking of measurements and the limit of accuracy, were as Pease⁴ has previously described. Pure carbon monoxide was obtained by the decomposition of formic acid and passage of the gas over phosphorus pentoxide and soda lime. The 63.42 grams

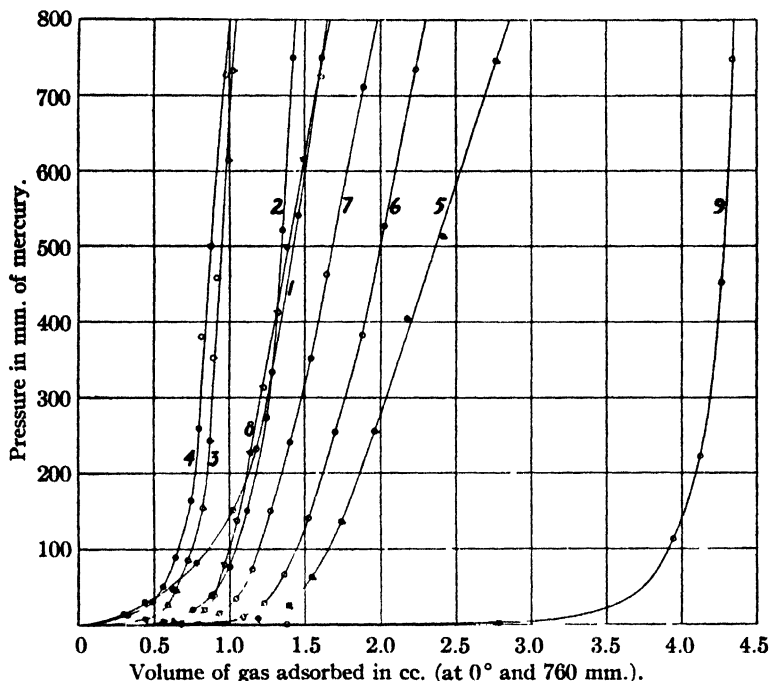
¹ Taylor and Burns, *THIS JOURNAL*, **43**, 1273 (1921).

² (a) Pease, *ibid.*, **45**, 1196 (1923); (b) **45**, 2296 (1923).

³ Pease and Stewart, *ibid.*, **47**, 1235 (1925).

⁴ Pease, *Refs.* 2 and 3.

of copper used was the second catalyst employed by Pease and Griffin⁵ and thus already established as permanently active to a high degree. The poison, carbon monoxide, was always introduced into the catalyst bulb approximately a half hour before a run was started. At the end of the run pumping out at 200° completely removed the hydrogen or ethylene and also the poison. Measurements were made at 20 and at 0°. Helium, assumed unadsorbed, was used as a reference gas.



Curve 1, H_2 with no CO; 2, H_2 with 0.038 cc. CO; 3, H_2 with 0.26 cc. CO; 4, H_2 with 0.74 cc. CO; 5, C_2H_4 with no CO; 6, C_2H_4 with 0.038 cc. CO; 7, C_2H_4 with 0.24 cc. CO; 8, C_2H_4 with 0.73 cc. CO; 9, pure CO.

Fig. 1.—Adsorptions of hydrogen and ethylene on copper poisoned with carbon monoxide at 0°. Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

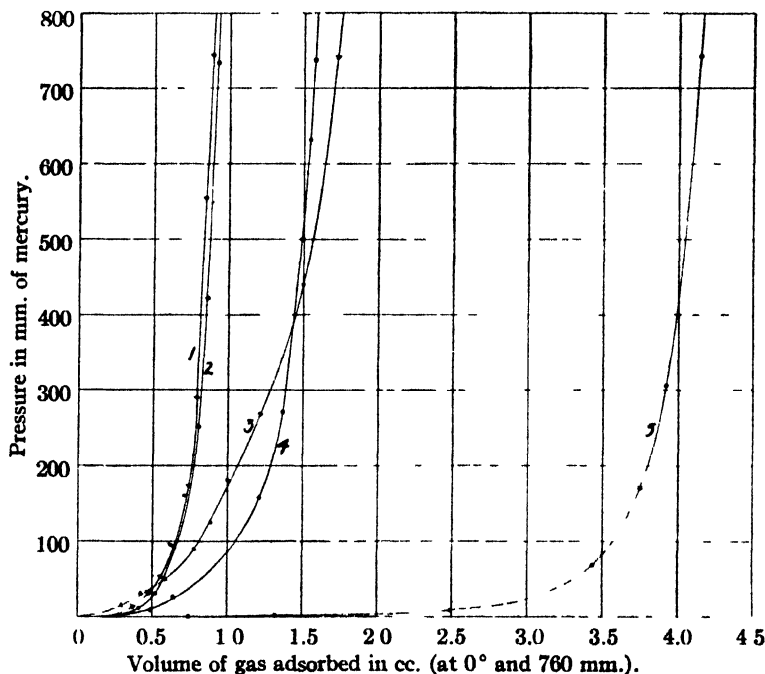
Adsorptions of the three gases on the pure catalyst were made first. Then hydrogen adsorption was alternated with ethylene on the catalyst poisoned first with 0.038 cc. of carbon monoxide and then with about 0.75 cc. and finally with about 0.25 cc. A run at 20° was always followed by the corresponding run at 0°.

Constancy of Activity.—Reaction velocity runs with 1:1 mixtures of ethylene and hydrogen were used as checks on the activity of the catalyst.

⁵ Pease and Griffin, *THIS JOURNAL*, 49, 25 (1927).

The first was made at the beginning of the investigation, another midway, and a third at the end of the research. Taking the activity of the first as 100%, the second proved to be 104% (based on the time required for the pressure to drop from 700 mm. to 600 mm.) and the third 108%. Due to the fact that the reaction velocity was very rapid (being practically completed in 7 minutes) these are considered as very satisfactory checks.

About a week after all the runs were completed a small crack occurred in the catalyst bulb, which allowed a very slight oxidation of the copper



Curve 1, H_2 with 0.76 cc CO; 2, H_2 with 0.27 cc. CO; 3, H_2 with no CO; 4, H_2 with 0.038 cc. CO; 5, pure CO.

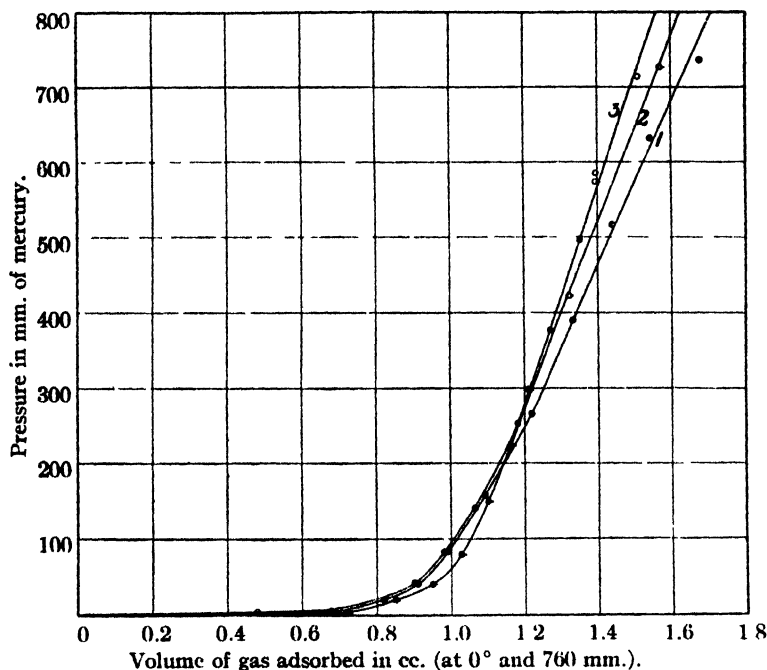
Fig. 2.—Adsorption of hydrogen on copper poisoned with carbon monoxide at 20° . Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

to take place. The crack was sealed and a new helium run was made. A subsequent reaction velocity run showed a less active catalyst, 64%, and an ethylene adsorption run at 20° following this showed an adsorption practically unchanged up to one-half atmosphere and only 7.8% less at one atmosphere. This confirmed the belief that reaction velocity is a more sensitive test of surface condition than adsorption, and that during the course of the investigation the catalyst remained substantially constant in both its catalytic and adsorptive activity.

Following experiments with this sample of copper, another sample

was used with which five runs were made. The first and last were ethylene runs on the pure sample, poisoned runs intervening. The adsorption activity was identical in the first and fifth runs.

It is noteworthy that throughout the first several runs, in addition to measurements made as gas was admitted to the catalyst bulb, portions of gas were withdrawn and readings taken. The points so secured fall on the curves with the same accuracy as those obtained when the gas was admitted, thus showing the absence of hysteresis.

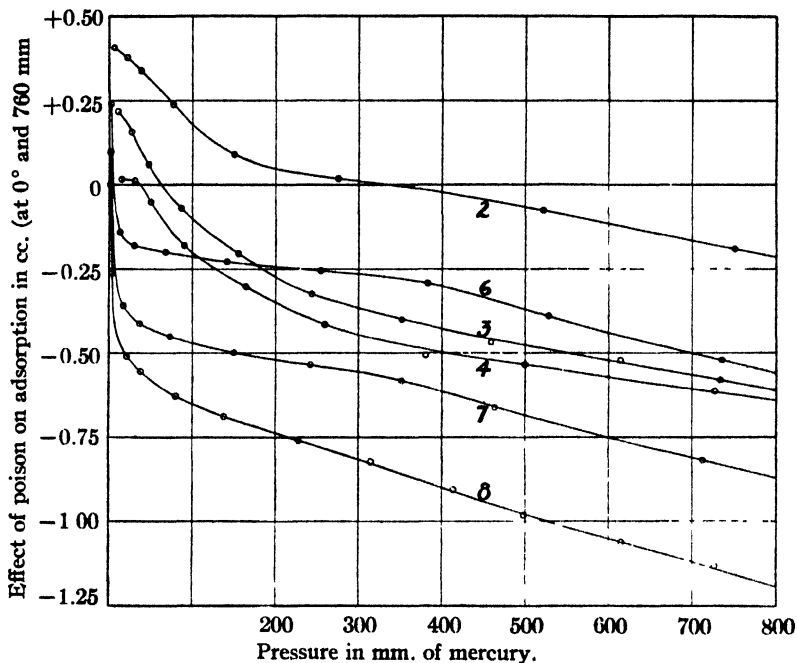


Curve 1, C_2H_4 with no CO; 2, C_2H_4 with 0.24 cc. CO; 3, C_2H_4 with 0.72 cc. CO.

Fig. 3.—Adsorption of ethylene on copper poisoned with carbon monoxide at 20° . Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

Results.—Adsorption isotherms at 0° are shown in Fig. 1. On the unpoisoned catalyst these are essentially the same as obtained by Pease. Curves 2, 3 and 4 for hydrogen and 6, 7 and 8 for ethylene show the effect of poisoning with progressively greater amounts of carbon monoxide. Considering for the moment higher pressures, it is noticed that both in the case of ethylene and hydrogen the effect of the poison is a progressive decrease of adsorption with increase of carbon monoxide. In the isotherms at 20° (shown for hydrogen in Fig. 2 and for ethylene in Fig. 3) at pressures of about a half to one atmosphere the same result is

found. In Figs. 2 and 3 it is seen that at lower pressures there is an *increase* of adsorption where poison was used. This increase diminishes as the pressure increases, the curve crossing the isotherm of the gas on the unpoisoned copper and representing thereafter a *decrease* in adsorption for the higher pressures. This increase of adsorption persists, in general, to higher pressures for hydrogen than for ethylene, and for either gas the smallest amount of poison causes the greatest increase of adsorption at low pressures and the least decrease of adsorption at high pressures.



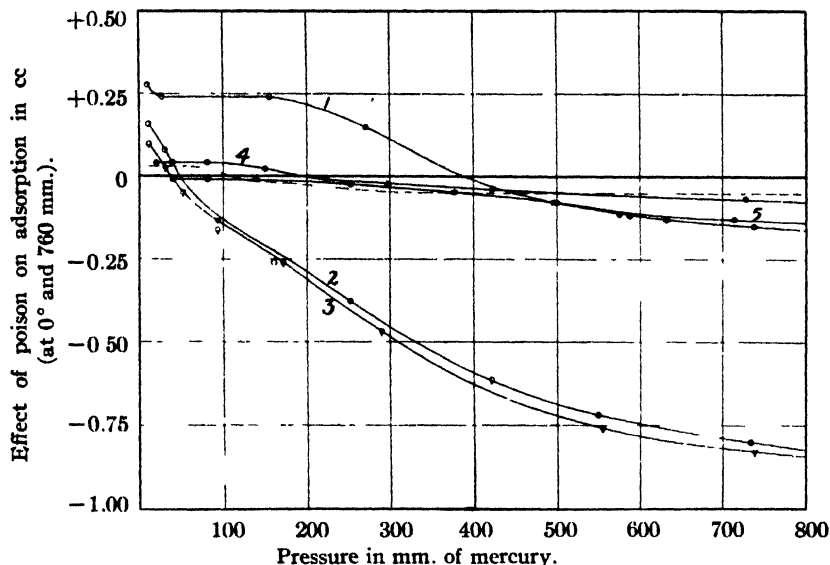
Curve 2, H_2 with 0.038 cc. CO; 3, H_2 with 0.26 cc. CO; 4, H_2 with 0.74 cc. CO; 6, C_2H_4 with 0.038 cc. CO; 7, C_2H_4 with 0.24 cc. CO; 8, C_2H_4 with 0.73 cc. CO.

Fig. 4.—Effect of poison on adsorption at 0°.

With one exception the same kind of behavior is found in the 0° curves, but in some cases the points at which the poison curves cross the unpoisoned isotherms are at such low pressures as probably not to be at once evident in Fig. 1. To bring out these considerations more distinctly, Figs. 4 and 5 are drawn in which pressure is plotted against $V_1 - V_2$, where V_1 is the volume of the gas adsorbed by the poisoned catalyst and V_2 is the volume of the gas adsorbed by the pure catalyst. The exception referred to above is the case of ethylene at 20° with 0.72 cc. of carbon monoxide as poison. Here at the lowest pressure measured there is already a decrease in adsorption due to the poison. By extrapolation,

however, it is evident that here also at very low pressure there is an increase over normal adsorption.

It will be noted that no curve is given for ethylene at 20° with 0.038 cc. of poison. Such a run was made; however, it was found to show a decrease in adsorption considerably greater than the run in which even 0.72 cc. of carbon monoxide had been used. Since such a result is not compatible with the research as a whole, it is believed that some unknown source of error entered this run. As calculations were not made until practically all the runs had been completed, this incongruity was not noticed until after the catalyst was no longer available. A new sample



Curve 1, H₂ with 0.038 cc. CO; 2, H₂ with 0.27 cc. CO; 3, H₂ with 0.76 cc. CO; 4, C₂H₄ with 0.24 cc. CO; 5, C₂H₄ with 0.72 cc. CO, broken line, C₂H₄ with 0.038 cc. CO (new catalyst).

Fig. 5.—Effect of poison on adsorption at 20°.

of copper oxide was later reduced and five runs made on the copper (125 g.) including a run of ethylene on the pure copper followed by a carbon monoxide run and then ethylene on the catalyst poisoned first with 0.038 cc. of carbon monoxide and then with 0.24 cc. The 0.038 cc. poison run showed a low-pressure increase of adsorption and a high-pressure decrease; the decrease, however, as had been expected, was less than that caused by 0.24 cc. of poison on the same catalyst. In Fig. 5 the effect of the 0.038 cc. of carbon monoxide on this new catalyst is shown by the broken curve. (This broken curve is the only one from the new catalyst. All other curves refer to the original catalyst.)

A reaction velocity measurement with a 1:1 mixture of ethylene and

hydrogen on the catalyst poisoned with 0.038 cc. carbon monoxide showed a decrease in catalytic activity of 80%, a fair check with the result of 88% obtained by Pease and Stewart⁴ with their catalyst.

Discussion of Results

The fact that the results of this work show as an effect of carbon monoxide poisoning an increase of low-pressure adsorption of hydrogen and ethylene is precisely the opposite of what was expected in view of the results of previous workers. Rather, it had been believed that isotherms similar to those found where mercury had been used as a poison or where the copper had been treated with heat would be obtained. It was even as great a surprise to find, whatever the effect, that it should be reversed at higher pressure.

Doubtless there are more ways than one of viewing these results. The low-pressure increase of adsorption due to the poison is quite definite, and even in those cases where the increase is only very slight and possibly within the magnitude of the experimental error, it is believed that they are nevertheless real and significant in view of the fact that without exception every run exhibited the low-pressure increase.

It is conceivable that the carbon monoxide simply caused a redistribution of adsorptive power among the active centers, altering the adsorption at various pressures without changing the number of centers and thus without changing appreciably the total, eventual adsorption at an indefinitely higher pressure. It hardly seems, however, that such reasoning could explain the results obtained, for it would then be difficult at least to explain a decrease of adsorption greater than the amount of poison added.

Inasmuch as the critical temperature of hydrogen is very low, namely, -234.5° , and qualitatively hydrogen and ethylene behave alike in their adsorption on the poisoned catalyst, it is evident that capillary condensation does not take place and thus any peculiar effect of the poison on that process is presumably out of the question.

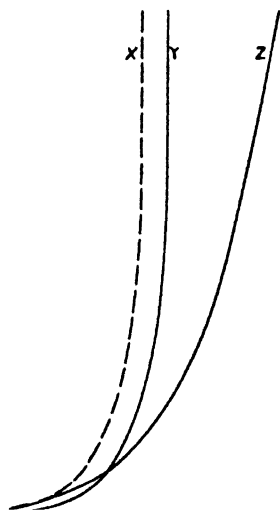
Therefore, it seems necessary to assume that an adsorbed carbon monoxide molecule is capable of linking several hydrogen or ethylene molecules, perhaps to itself, perhaps by increasing the activity of neighboring centers, or possibly both. If this is true then the results may be looked upon as follows. The carbon monoxide must be adsorbed on the very active centers in view of the marked decrease in catalytic activity caused by an extremely small amount of poison. The carbon monoxide thereafter takes up hydrogen or ethylene molecules to such an extent that the total adsorption at a given low pressure is greater than on the unpoisoned catalyst where each very active point presumably holds only one molecule. This could explain that part of the curve showing an increase of adsorption.

It is difficult to say why an increase of adsorption should at higher pressure give way to a decrease. The accumulation of more and more data on the subject of adsorption seems to indicate that the process probably is complex, involving not simply one kind of action but nearly always several agencies, all included under the term sorption. It may be true that in the case of ethylene and hydrogen on copper, the measurements made have not been a record of adsorption, pure and simple. In the case in hand, possibly in addition to adsorption of the gases on the surface, actual solution of the gases is involved. If solution actually did take place it might indicate the presence of more or less amorphous copper. Rideal⁶ assumes the presence of the amorphous form in such samples as have been employed by Pease; he even supposes the strongest catalytically active centers of copper to be amorphous "patches."

It is true that Sieverts'⁷ studies do not indicate solution of hydrogen in copper at the temperatures of 20 and 0°. However, Sieverts used electrolytic copper wire, whereas that employed in this research was obtained by slow reduction of copper oxide at 150°.

Assuming a secondary action in addition to that of straight adsorption, Curve X of Fig. 6 could represent that due strictly to adsorption. Curve Z would represent the sorption actually observed on the pure catalyst and due to surface adsorption plus the secondary action. If the secondary action were that of solution it would be negligible at low pressure and thus practically coincident with Curve X in that region. One would expect the increase of surface adsorption due to the poison to continue at all pressures. If, in addition, the poison prevents the solution process, the sorption on the poisoned catalyst would be represented by Curve Y. Curves Z and Y represent what actually are found on the pure and on the poisoned catalyst, respectively, while Curves X and Y represent what might be found were the secondary action absent.

Suppose the secondary factor to be solution. If the carbon monoxide attaches little or no more hydrogen at higher pressures than at zero pressure, and were the amount dissolved unaffected, then the curves of Figs.



Volume of sorption.

Fig. 6.

⁶ Rideal, "Surface Chemistry," Cambridge University Press, 1926, p. 183.

⁷ Sieverts, *Z. physik. Chem.*, 60, 145 (1907).

4 and 5 would be horizontal lines. The vertical distances between such a line and the actual curve at a given pressure would represent the difference in the amount of gas dissolved in the pure copper and in the poisoned copper. By extrapolating the three hydrogen curves of Fig. 4 to zero pressure and arithmetically adding to these values the corresponding decrease at 700 mm. pressure, the result is roughly 0.60 cc. for the smallest amount of poison and 0.85 cc. for each of the two larger amounts. Such a relation indicates that 0.038 cc. of the poison was almost enough and 0.26 cc. or 0.74 cc. entirely sufficient to prevent solution. At 20° (Fig. 5) the hydrogen curve for 0.038 cc. of poison exhibits a relatively slight difference of solution compared to that of the unpoisoned copper, and the curves for the two larger amounts of poison show diminutions practically identical in themselves but much greater than that for the smallest quantity of poison. Comparison of hydrogen curves at 0 and 20° in Figs. 4 and 5 shows that the solubility is slightly greater at 20 than at 0°, as would be expected. With the larger amounts of poison the solubility difference between pure and poisoned copper is about 0.98 cc. at 20° as compared with 0.85 cc. at 0°. The approximately parabolic form of these curves indicates that the solubility is proportional to the square root of the pressure as Sieverts and Krumbhaar⁸ found to be the case for hydrogen in copper at higher temperatures.

That a very small quantity of poison is sufficient to prevent solution in the copper may be attributed to its ability to incapacitate the very active centers on the copper surface, thereby depriving the molecular hydrogen of its dissociating agency. The nature of the ethylene curves differs from that of hydrogen chiefly in that at 0° they bend more abruptly in approaching zero pressure. Without further hypothesizing it is, therefore, difficult to draw similar conclusions for ethylene.

It appears that a different attack on the problem presented by this investigation may be pursued, since a supported catalyst should largely do away with all except surface adsorption, and it seems that much might be learned by poisoning such a catalyst. It is planned to investigate this possibility.

Finally, it should be mentioned that it appears now more certainly than ever that adsorptions even at very low pressures do not serve as a measure of catalytic activity. Furthermore, it should be recorded that those molecules of hydrogen or ethylene which give the low-pressure increase of adsorption—that is, those molecules which owe their linkage to the poison itself, either directly or indirectly—are *not* activated. That this is definitely a fact is evidenced by the catalytic inactivity of the poisoned copper, for although in the low-pressure region the adsorption of both gases is actually increased by the poison, nevertheless the copper is practically inert as a catalyst.

⁸ Sieverts and Krumbhaar, *Z. physik. Chem.*, **74**, 277 (1910).

The writer wishes to express his heartiest thanks to Dr. A. F. Benton, whose frequent advice was of great value.

Summary

1. Adsorption measurements have been made for ethylene and hydrogen on a copper catalyst poisoned with carbon monoxide.

2. It has been found that the poison causes a low-pressure increase and a high-pressure decrease of adsorption as compared to measurements made on the unpoisoned catalyst. The poison decreases the catalytic activity very markedly.

3. A possible, general interpretation of the results has been outlined, assuming the process of sorption to comprise a secondary factor such as solution in addition to surface adsorption.

4. It has been shown that carbon monoxide in causing extra, low-pressure sorption of the gases does not leave the hydrogen or ethylene in an activated state.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PHOTOCHEMICAL REARRANGEMENT OF ACETYLCHLORO-AMINO BENZENE

BY C. W. PORTER AND PAUL WILBUR

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The photochemical rearrangement of acetylchloro-aminobenzene to *p*-chloro-acetanilide has been the subject of many investigations, but heretofore the absorption coefficients in the region of effective radiation have not been determined. A study of factors governing the rearrangement in the solid phase has not been made, although Slosson¹ long ago reported the observation that heat alone causes the change. The rearrangement in the presence of various solvents has received careful attention.²

We have undertaken to measure the energy required to convert one molecule of the chloro-amine into the isomeric form. As a preliminary step we determined the absorption coefficients of acetylchloro-aminobenzene and of the *p*-chloro-acetanilide over the range between 2200 and 3400 Ångström units. These results, with some observations relating to the rearrangement in the solid phase, are presented in this paper. The energy measurements which have been made on the absorption of certain narrow bands in the spectrum will be published after we have made further attempts to obtain results with pure monochromatic light.

The absorption coefficients were determined as follows. The spectrum

¹ Slosson, *Am. Chem. J.*, **29**, 289 (1903).

² (a) Acree and Johnson, *Am. Chem. J.*, **37**, 258 (1907); (b) Rivett, *Z. physik. Chem.*, **82**, 201 (1913); (c) Mathews and Williamson, *THIS JOURNAL*, **45**, 2574 (1923).

of the mercury-vapor arc was photographed through a quartz cell containing the pure solvent (conductivity water) and through copper gauze screens. On the same plate, and with equal exposures for corresponding pairs, other series of photographs were made with the screens removed and with the quartz cell filled with solutions of known concentrations of the substance under investigation. The fraction of the total incident light which passed through each screen had been determined in advance by photometric measurements in the visible region. The logarithm of the reciprocal of this ratio is the value of ecd in the statement of Beer's law, $I_t/I_0 = 10^{-ecd}$.

Points of equal degrees of blackening on two photographs on the same plate, one taken through a screen of known absorption, and the other through a solution of known concentration, c , and known depth, d , correspond to frequencies where the two systems have the same absorption coefficient, e .

TABLE I

SOLUTIONS OF ACETYLCHLORO-AMINO BENZENE

Plate I: $c = 0.001 M$ Plate II: $c = 0.0001 M$

$\lambda \pm 3 \text{ \AA.}$	$\text{Log } \frac{I_t}{I_0}$	e	$\lambda \pm 3 \text{ \AA.}$	$\text{Log } \frac{I_t}{I_0}$	e
3377	0.159	30	2944	0.31	590
3258	.310	59	2838	.48	914
3189	.480	91	2744	.67	1286
3144	.675	128	2630	.93	1785
3108	.927	178	2562	1.20	2285
3074	1.20	228	2549	1.35	2571
3059	1.35	257	2406	4.80	4571 ^a

^a From Plate IV, $c = 0.00002 M$.

TABLE II

SOLUTIONS OF *p*-CHLORO-ACETANILIDEPlate V: $c = 0.001 M$ Plate VI: $c = 0.0001 M$

$\lambda \pm 3 \text{ \AA.}$	$\text{Log } \frac{I_t}{I_0}$	e	$\lambda \pm 3 \text{ \AA.}$	$\text{Log } \frac{I_t}{I_0}$	e
2978	0.159	30	2842	0.31	590
2950	.310	59	2777	.48	914
2934	.480	91	2738	.67	1286
2920	.675	128	2716	.93	1785
2912	.937	178	2699	1.20	2285
2900	1.20	228	2688	1.35	2571

Partial data from Plates VII, VIII, IX, X: $c = 0.00002 M$

$\lambda \pm 3 \text{ \AA.}$	$e \times 10^{-3}$	$\lambda \pm 5 \text{ \AA.}$	$e \times 10^{-3}$	$\lambda \pm 10 \text{ \AA.}$	$e \times 10^{-3}$
2682	29	2562	99	2340	99
2649	45	2545	114	2308	89
2628	53	2516	128	2283	84
2614	64	2430	142	2253	64
2594	71	2377	128	2242	59
2581	89	2351	114	2230	53

The points of equal densities were determined by projecting the images of the photographic negatives on a vacuum thermopile and finding positions that caused equal galvanometer deflections.³ The wave lengths corresponding to these points of equal intensities were determined by reference to known lines in the mercury spectrum. In all cases the measurements were made at temperatures between 22 and 25°. The length of the quartz cell containing the solutions was 5.25 cm. The solvent was water. The photographs were taken through a Hilger quartz prism spectrograph.

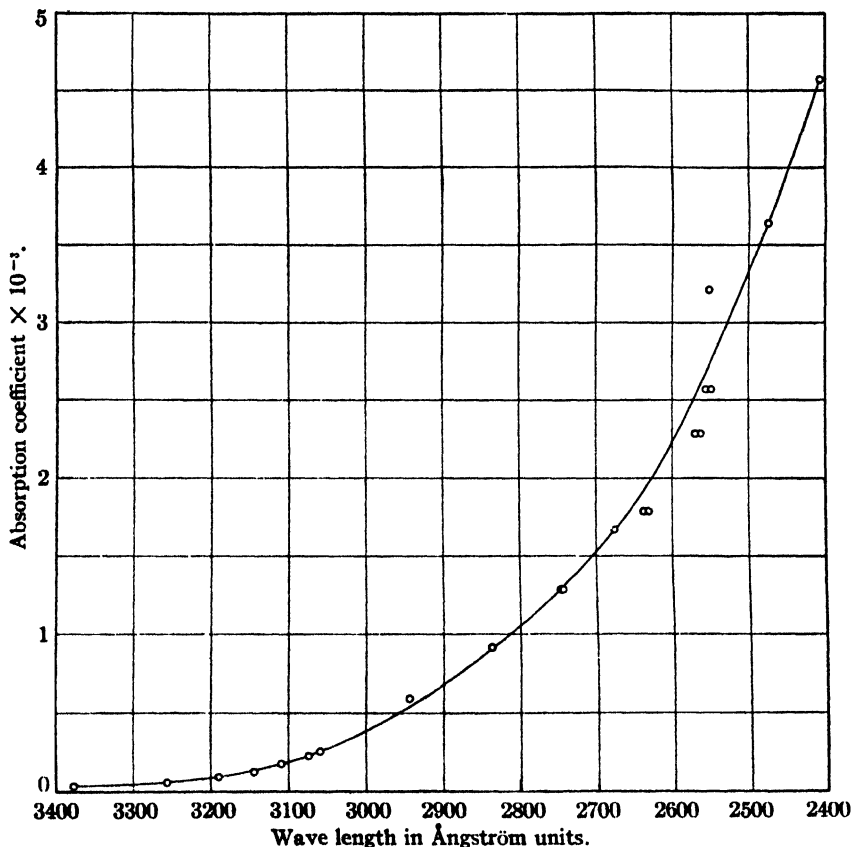


Fig. 1.

These values, together with some data obtained from several other plates, are shown in Figs. 1 and 2. Values referring to points that could not be determined within 10 Å. are, of course, only approximations.

Pure, dry crystals of acetylchloro-aminobenzene, when exposed to the radiation of a mercury-vapor lamp, are converted rapidly into *p*-chloro-

³ Ramsperger and Porter, *THIS JOURNAL*, 48, 1267 (1926).

acetanilide. A 90 per cent. conversion was made within eight hours by placing a thin layer of the crystals in an open dish at a distance of 20 cm. below a 220-volt lamp.

The same change can be induced by heat alone. The reaction is slow unless the acetylchloro-aminobenzene is heated to its melting point. Above the melting point the change is rapid, but it is not possible to maintain a constant temperature within the molten mass. The energy of the reaction causes local heating and an acceleration of rate until finally the rearrangement is completed with almost explosive rapidity.

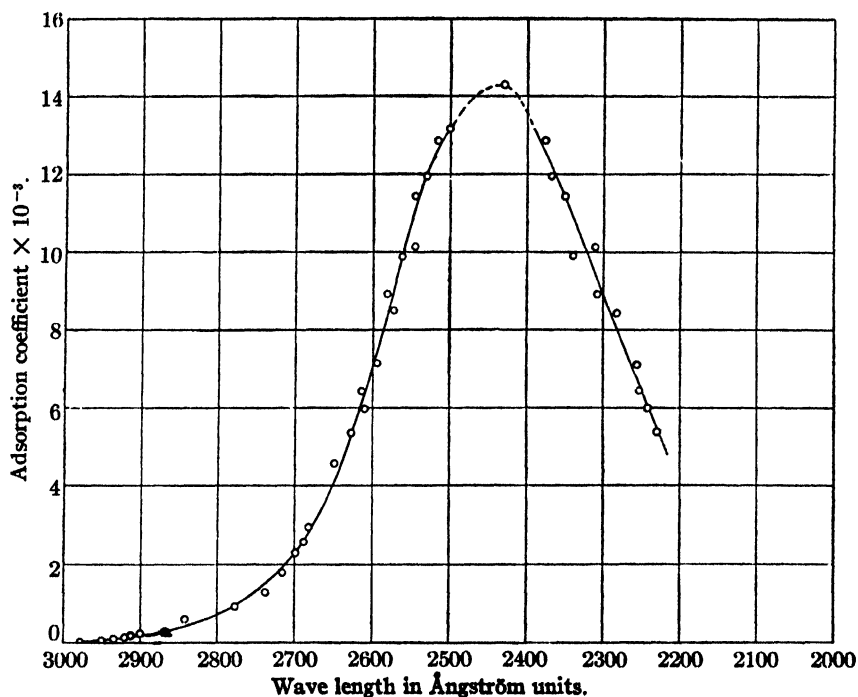


Fig. 2.

Sealed tubes containing the crystalline solid were immersed in a water-bath at 100°. The crystals melted immediately, but within two hours the material had again become solid, due to complete conversion to the higher-melting product. No nitrogen was evolved in the process and, although slight discoloration was sometimes observed, the product was always found to be almost exclusively *p*-chloro-acetanilide.

The claim that the conversion of acetylchloro-aminobenzene into *p*-chloro-acetanilide is actually a rearrangement has been challenged under the assumption that it is a two- or three-stage process.⁴ Many

⁴ Kipping, Orton and others, *Chem. News*, 108, 155 (1913).

mechanisms involving the formation of intermediate products with the solvent or with an added catalyst have been proposed.

While these mechanisms may apply to the reaction in the specified environment, they certainly do not describe the behavior of the compound in the dry state. A direct unimolecular exchange of positions between the amino halogen and nuclear hydrogen seems to be the simplest assumption in connection with the photochemical rearrangement of the pure, dry crystals.

Summary

The ultraviolet absorption spectrum of acetylchloro-aminobenzene and of its rearrangement product, *p*-chloro-acetanilide, has been plotted.

The rearrangement is caused by heat alone at comparatively low temperatures. The reaction is completed within two hours at 100°.

The rearrangement occurs in the absence of solvents and without the appearance of a liquid phase when solid crystals of acetylchloro-aminobenzene are exposed to the radiation of a mercury-vapor lamp.

Mechanisms involving intermediate products cannot apply to the solid phase reaction.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 134]

THE CRYSTAL STRUCTURES OF AMMONIUM, POTASSIUM AND RUBIDIUM CUPRIC CHLORIDE DIHYDRATES

BY STERLING B. HENDRICKS AND ROSCOE G. DICKINSON

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Introduction

The low crystallographic symmetry of most salt hydrates and ammoniates has prevented the study of such compounds by x-ray methods. In an effort to comprehend more fully the geometrical relationship of water to the other components of such compounds we have studied the alkali cupric chloride dihydrates, $R_2CuCl_4 \cdot 2H_2O$ (where R represents ammonium, potassium or rubidium). These compounds form an apparently isomorphous series crystallizing in the ditetragonal bipyramidal class of the tetragonal system.¹ The axial ratios and observed densities of these compounds are given in Table I.

Large crystals, showing development of (111) and (100), were grown from aqueous solutions containing cupric chloride and the alkali chloride in the correct stoichiometrical quantities. Great caution was used in selecting crystals for the x-ray photographs, since twinning on (111)

¹ Groth, "Chemische Krystallographie" Engelmann, Leipzig, 1906, vol. I, pp. 355-356.

TABLE I

AXIAL RATIOS AND DENSITIES OF THE ALKALI CUPRIC CHLORIDE DIHYDRATES

Compound	Axial ratio $a:c$		Density	
	Goniometric	X-ray	Obs.	Calcd.
$K_2CuCl_4 \cdot 2H_2O$	1:0.7525	1:0.7405	2.410	2.41
$(NH_4)_2CuCl_4 \cdot 2H_2O$	1:0.7417	1:0.7415	2.01 (1.963)	1.98
$Rb_2CuCl_4 \cdot 2H_2O$	1:0.7441	1:0.7250	2.895	2.80

was common. The investigation was carried out by the use chiefly of Laue and spectral photographs interpreted with the aid of the theory of space groups.²

The Structure of Potassium Cupric Chloride Dihydrate

The Unit of Structure.—Spectral data for $K_2CuCl_4 \cdot 2H_2O$ are listed in Table II, and for the ammonium and rubidium salts in Tables III and IV, respectively. Col. 1 gives the crystallographic indices of the face under consideration; those without subscript refer to the original crystallographic axes, while indices with the subscript s. g. refer to the axes of the unit of structure. The angles of reflection, θ , of molybdenum K lines are given in Col. 4. For potassium cupric chloride dihydrate the smallest unit compatible with these spectral data has its a axis rotated 45° from the original crystallographic axis, and has $d_{100} = d_{010} = 7.45 \text{ \AA.}$ and $d_{001} = 7.88 \text{ \AA.}$ It contains $2.00 K_2CuCl_4 \cdot 2H_2O$. The method described by Kirkpatrick and Dickinson³ was used in making this restriction. No Laue data were found requiring a larger unit.

TABLE II

SPECTRAL DATA FROM $K_2CuCl_4 \cdot 2H_2O$

hkl	Order	Line (a)	Angle of reflection	d/n	Obs. intensity	Calcd. structure factor
(111)	$n (= 1)$	MoK β	$2^\circ 53'$	5.420	m. w.	69
(101) _{s. g.}	n	α	$3^\circ 15'$	5.420	s.	
	$2n$	γ	$5^\circ 40'$	5.418	w.	
	$2n$	β	$5^\circ 47.5'$	5.404	m.	162
	$2n$	α	$6^\circ 32.5'$	5.395	v. s.	
	$3n$	β	$8^\circ 44'$	5.391	v. v. w.	73
	$3n$	α	$9^\circ 48.5'$	5.410	w.-m. w.	
	$4n$	γ	$11^\circ 26'$	5.395	v. w.	
	$4n$	β	$11^\circ 37.5'$	5.413	m. w.	225
	$4n$	α_1	$13^\circ 5'$	5.410	m. s.	
	$4n$	α_2	$13^\circ 12.5'$	5.407	m.	
(001)	$n (= 2)$	β	$3^\circ 58'$	3.899	m. w.	
(001) _{s. g.}	n	α	$4^\circ 28.5'$	3.938	s.	94
	$2n$	γ	$7^\circ 47'$	3.948	w.-v. w.	

² For a detailed description of the experimental methods see Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, 1924, pp. 109-116, 161-164.

³ Kirkpatrick and Dickinson, THIS JOURNAL, 48, 2327 (1926).

TABLE II (Concluded)

hkl	Order	Line (a)	Angle of reflection	d/n	Obs. intensity	Calcd. structure factor
	$2n$	β	$7^{\circ}57'$	3.945	m.	
	$2n$	α_1	$8^{\circ}58'$	3.931	v. s.	264
	$2n$	α_2	$9^{\circ}1'$	3.935	m. s.	
	$3n$	β	$12^{\circ}0'$	3.932	v. v. w.	
	$3n$	α_1	$13^{\circ}28'$	3.943	w.	84
	$3n$	α_2	$13^{\circ}35'$	3.940	v. w.	
	$4n$	β	$16^{\circ}3'$	3.944	v. v. w.	
	$4n$	α_1	$18^{\circ}4.5'$	3.945	m.-m. w.	234
	$4n$	α_2	$18^{\circ}10'$	3.955	w.	
(110)	$n (= 2)$	β	$4^{\circ}13'$	3.706	v. w.	52
(100) _{a. g.}	n	α	$4^{\circ}46'$	3.699	m. w.	
	$2n$	γ	$8^{\circ}16.5'$	3.715	w.	
	$2n$	β	$8^{\circ}24'$	3.731	m.	256
	$2n$	α	$9^{\circ}29.5'$	3.726	v. s.	
(100)	$n (= 1)$	α	$3^{\circ}25'$	5.156	w.	29
(110) _{a. g.}	$2n$	γ	$5^{\circ}51'$	5.241	w.	
	$2n$	β	$5^{\circ}58'$	5.241	s.	283
	$2n$	α	$6^{\circ}42'$	5.270	v. s.	
	$3n$	α	$10^{\circ}5'$	5.270	w.	73
	$4n$	γ	$11^{\circ}50'$	5.218	v. w.	
	$4n$	β	$11^{\circ}57'$	5.260	w.	225
	$4n$	α_1	$13^{\circ}26'$	5.270	m.	
	$4n$	α_2	$13^{\circ}32'$	5.270	m. w.	

In the tables concerning the spectral data the following abbreviations and simplifications are used: (a) $MoK\beta = 0.6311 \text{ \AA.}$; $K\gamma = 0.6178 \text{ \AA.}$; $K\alpha_1 = 0.7078 \text{ \AA.}$; $K\alpha_2 = 0.7120 \text{ \AA.}$; K_{α} , mean of K_{α_1} and K_{α_2} , 0.710 \AA. ; (b) v. v. w. = very, very weak; v. w. = very weak; w. = weak; m. w. = medium weak; m. = medium; m. s. = medium strong; s = strong; v. s. = very strong.

TABLE III
SPECTRAL DATA FROM $(NH_4)_2CuCl_4 \cdot 2H_2O$

hkl	Order	Line	Angle of reflection	d/n	Obs. intensity	Calcd. structure factor
(111)	$n (= 1)$	β	$3^{\circ}15'$	5.565	v. w.	69
(101) _{a. g.}	n	α	$3^{\circ}40.5'$	5.539	m.	
	$2n$	γ	$6^{\circ}28'$	5.500	v. w.	
	$2n$	β	$6^{\circ}34'$	5.519	m.	132
	$2n$	α_1	$7^{\circ}23'$	5.505	s.	
	$2n$	α_2	$7^{\circ}24.5'$	5.520	m.	
	$3n$	β	$9^{\circ}56.5'$	5.481	v. w.	13
	$3n$	α	$11^{\circ}9.5'$	5.505	w.	
	$4n$	γ	$13^{\circ}2.5'$	5.491	v. w.	
	$4n$	β	$13^{\circ}17.5'$	5.490	m. w.	168
	$4n$	α_1	$14^{\circ}56'$	5.514	s.	
	$4n$	α_2	$15^{\circ}15'$	5.493	m.	
(001)	$n (= 2)$	γ	$4^{\circ}27'$	3.994	v. w.	
(001) _{a. g.}	n	β	$4^{\circ}31.5'$	3.999	w.	126
	n	α	$5^{\circ}6.5'$	3.990	m. s.	
	$2n$	γ	$8^{\circ}57.5'$	3.981	v. w.	

TABLE III (Concluded)

<i>hkl</i>	Order	Line	Angle of reflection	<i>d/n</i>	Obs. intensity	Calcd. structure factor
	$2n$	β	$9^{\circ}7.5'$	3.981	m.	232
	$2n$	α_1	$10^{\circ}15.5'$	3.978	s.	
	$2n$	α_2	$10^{\circ}18.5'$	3.980	m.	
	$3n$	β	$13^{\circ}46'$	3.980	v. w.	
	$3n$	α_1	$15^{\circ}29'$	3.978	w.	116
	$3n$	α_2	$15^{\circ}35.5'$	3.978	v. w.	
(100)	$n (= 1)$	β	$3^{\circ}19'$	5.360	v. w.	61
(110) _{s. g.}	n	α	$3^{\circ}45'$...	m.	
	$2n$	γ	$6^{\circ}37.5'$	5.370	w.	
	$2n$	β	$6^{\circ}44'$	5.380	m. s.	251
	$2n$	α	$7^{\circ}36.5'$	5.364	v. s.	
	$3n$	β	$10^{\circ}11.5'$	5.358	v. w.	
	$3n$	α_1	$11^{\circ}26.5'$	5.355	m.	107
	$3n$	α_2	$11^{\circ}29'$	5.371	w.	
	$4n$	β	$13^{\circ}37'$	5.361	v. w.	
	$4n$	α_1	$15^{\circ}17.5'$	5.365	m.	193
	$4n$	α_2	$15^{\circ}24'$	5.370	w.	

TABLE IV

SPECTRAL DATA FROM $\text{Rb}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$

<i>hkl</i>	Order	Line	Angle of reflection	<i>d/n</i>	Obs. intensity	Calcd. structure factor
(111)	$n (= 1)$	β	$3^{\circ}17.5'$	5.494	v. v. w.	69
(101) _{s. g.}	n	α	$3^{\circ}43'$	5.488	v. w.	
	$2n$	γ	$6^{\circ}31'$	5.465	v. v. w.	
	$2n$	β	$6^{\circ}37'$	5.485	w.-v. w.	236
	$2n$	α_1	$7^{\circ}24'$	5.494	m.	
	$2n$	α_2	$7^{\circ}27.5'$	5.483	w.	
	$3n$	abs.	13
	$4n$	β	$13^{\circ}15.5'$	5.500	v. w.	
	$4n$	α_1	$14^{\circ}53'$	5.503	m. w.	282
	$4n$	α_2	$14^{\circ}59'$	5.503	w.	
(100)	$n (= 1)$	abs.	43
(110) _{s. g.}	$2n$	γ	$6^{\circ}27'$	5.515	v. v. w.	
	$2n$	β	$6^{\circ}34'$	5.520	v. w.	355
	$2n$	α_1	$7^{\circ}22'$	5.520	m.	
	$2n$	α_2	$7^{\circ}26'$	5.515	w.	
	$3n$	abs.	1
	$4n$	β	$13^{\circ}13.5'$	5.520	v. w.	
	$4n$	α_1	$14^{\circ}51.5'$	5.520	m. w.	297
	$4n$	α_2	$14^{\circ}57.5'$	5.520	w.	
(001)	$n (= 2)$	abs.	22
(001) _{s. g.}	$2n$	γ	$8^{\circ}53.5'$	4.010	v. w.	
	$2n$	β	$9^{\circ}5'$	3.995	m.	336
	$2n$	α_2	$10^{\circ}11'$	4.002	v. s.	
	$2n$	α_1	$10^{\circ}15'$	4.000	s.	

The Lattice and Space Group.—The observation that a Laue photograph made with the x-ray beam normal to (001) shows a fourfold axis

and four planes of symmetry requires the structure to be isomorphous with point group V_d , C_{4v} , D_4 or D_{4h} . The presence of reflections in the first order from planes with $h + k + l$ both odd and even as well as with $h + k$ both odd and even requires the lattice to be the simple tetragonal one Γ_1 . The following space groups based on this lattice and isomorphous with one of the above point groups are eliminated for the reasons given.⁴

TABLE V
LAUE PHOTOGRAPHIC DATA FROM $K_2CuCl_4 \cdot 2H_2O$, USED IN SPACE-GROUP
DETERMINATION
Photograph 1

Plane	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity
$\bar{2}30$	2.065	0.37	0.8
401	1.815	.42	.0
$\bar{4}10$	1.807	.36	4.0
331	1.712	.41	0.15
051	1.465	.45	2.5
061	1.225	.33	0.0
071	1.055	.35	1.5
$\bar{5}51$	1.045	.48	0.10
702	1.025	.31	.0
801	0.925	.43	.0

Photograph 2

10 $\bar{4}$	1.907	.475	0
01 $\bar{4}$	1.907	.380	0
01 $\bar{7}$	1.112	.360	1.0
207	1.077	.324	0
02 $\bar{7}$	1.077	.250	0
$\bar{1}08$	0.976	.332	0
650	.953	.340	0 10
30 $\bar{8}$.916	.366	0
03 $\bar{8}$.916	.302	0
209	.852	.260	0
029	.852	.392	0
40 $\bar{9}$.792	.265	0
05 $\bar{9}$.756	.380	0.17

D_{4h}^8 , D_{4h}^{11} , D_{4h}^{13} , D_{4h}^{16} , C_{4v}^8 , D_4^3 , D_4^4 , D_4^7 and D_4^8 , since these space groups do not have positions for two copper atoms.

D_{4h}^3 , D_{4h}^4 , D_{4h}^7 , D_{4h}^8 , D_{4h}^{11} , D_{4h}^{12} , D_{4h}^{15} and D_{4h}^{16} , since these require the absence in odd orders of $(h\bar{k}0)$ with $(h+k)$ odd; yet $(\bar{4}10)$, $(\bar{2}30)$, (650) were observed to be present in the first order.

D_{4h}^5 , D_{4h}^6 , D_{4h}^{11} , D_{4h}^{13} , C_{4v}^2 , C_{4v}^3 require the absence in odd orders of $(0kl)$ if k is odd; $(0\bar{7}1)$, (051) , $(05\bar{9})$ and $(01\bar{7})$ were observed in the first order.

D_{4h}^2 , D_{4h}^8 , D_{4h}^{10} , D_{4h}^{16} , C_{4v}^4 , C_{4v}^5 require the absence in odd orders of $(0kl)$ if l is odd; $(0\bar{7}1)$, (051) , $(05\bar{9})$, $(01\bar{7})$ were observed in the first order.

⁴ Astbury and Yardley, *Phil. Trans.*, **224A**, 221 (1924).

D_{4h}^2 , D_{4h}^4 , D_{4h}^6 , D_{4h}^8 , D_{4h}^9 , D_{4h}^{11} , D_{4h}^{13} , D_{4h}^{15} , C_{4v}^5 , C_{4v}^6 , C_{4v}^7 , C_{4v}^8 , V_d^2 and V_d^4 require the absence of odd order reflection form (hkl) with l odd; (331) and (551) were observed in the first order.

D_4^3 , D_4^4 , D_4^7 and D_4^8 require the absence of (001) in even orders not multiples of four; the second and sixth orders were observed.

Space groups not eliminated by the above considerations require the following general absences of reflection in odd orders: D_{4h}^{14} , D_{4h}^{14} , C_{4v}^{14} , V_d^1 none; D_{4h}^{14} , C_{4v}^{14} , $(0kl)$ with $(k+l)$ odd; V_d^3 , D_4^2 , D_4^5 , (100), D_4^5 , (001). The types of absences of first-order reflections required by D_{4h}^5 , V_d^3 , D_4^2 and D_4^5 are special cases of those required to be absent by D_{4h}^{14} and C_{4v}^{14} , that is, reflection in the *odd* orders from planes of the type $(0kl)$ with $(k+l)$ odd. No such planes were found to reflect. Reflections in odd orders were found to be absent from the following planes: (160), (001), ($\bar{8}01$), ($\bar{1}08$), (061), (702), (401), ($10\bar{4}$), ($30\bar{8}$), ($20\bar{7}$), ($40\bar{9}$), ($02\bar{9}$). Examination of the coördinate positions in space groups D_{4h}^{14} , D_4^1 , C_{4v}^{14} , V_d^1 , V_d^3 , D_4^2 , D_4^5 and D_4^5 showed that this criterion could be satisfied in a few special cases, but that the absence of reflection would be dependent on a relationship involving relative reflecting powers and parameters defining atomic positions. While such a relationship might be satisfied for one member of the isomorphous series, it probably would not give a satisfactory answer for another member, the postulate being made that great changes in structure do not take place between different members of this isomorphous series. Accordingly D_{4h}^{14} and C_{4v}^{14} , which have the same general criteria, alone remain. On account of the difficulty of treating C_{4v}^{14} further, the remainder of the investigation has been confined to the more symmetrical space group D_{4h}^{14} . The justification for this is that D_{4h}^{14} is in accord with such crystallographic evidence as we possess and leads to a structure in agreement with our x-ray data.

The Atomic Arrangement.—The following are all the special arrangements⁵ occurring in D_{4h}^{14} ; the general arrangement possesses 16 equivalent positions and does not concern us here.

D_{4h}^{14}	Two equiv. positions	(a) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	(b) $00\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
	Four equiv. positions	(c) $0\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}00$	
		(d) $0\frac{1}{2}\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$	
		(e) $00w$; $00\bar{w}$; $\frac{1}{2}\frac{1}{2}w + \frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\bar{w} - \frac{1}{2}$	
		(f) $uu0$; $\bar{u}\bar{u}0$; $\frac{1}{2} - u, u + \frac{1}{2}, \frac{1}{2}$; $u + \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2}$	
		(g) $vv\frac{1}{2}$; $\bar{v}\bar{v}\frac{1}{2}$; $\frac{1}{2} - v, v + \frac{1}{2}, 0$; $v + \frac{1}{2}, \frac{1}{2} - v, 0$	
	Eight equiv. positions	(h) $0\frac{1}{2}u$; $\frac{1}{2}0u$; $\frac{1}{2}, 0, u + \frac{1}{2}$; $0, \frac{1}{2}, u + \frac{1}{2}$; $0\frac{1}{2}\bar{u}$; $\frac{1}{2}0\bar{u}$; $\frac{1}{2}, 0, \bar{u} - u$; $0, \frac{1}{2}, \bar{u} - u$	
		(i) $uv0$; $\bar{v}u0$; $v + \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2}$; $u + \frac{1}{2}, \frac{1}{2} - v, \frac{1}{2}$; $\bar{u}\bar{v}0$; $\bar{v}\bar{u}0$; $\frac{1}{2} - v, u + \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2} - u, v + \frac{1}{2}, \frac{1}{2}$	
		(j) uuv ; $uu\bar{v}$; $u + \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2} - v$; $u + \frac{1}{2}, \frac{1}{2} - u, v + \frac{1}{2}$; $\bar{u}\bar{u}\bar{v}$; $\bar{u}\bar{u}v$; $\frac{1}{2} - u, u + \frac{1}{2}, v + \frac{1}{2}$; $\frac{1}{2} - u, u + \frac{1}{2}, \bar{v} - v$	

⁵ Wyckoff, *Carnegie Inst. Pub.*, 318, p. 97 (1922).

The completion of the structure determination requires the allocation of 2 Cu, 4 alkali, 8 Cl and 4 H₂O among the above coördinates, and the determination of the parameters involved. The large number of possible combinations of these coördinates makes this task at first sight hopeless. Fortunately, however, we have found a general characteristic of the reflections from one class of planes, which greatly simplifies the problem. This observation is that first-order reflections from planes with $h + k + l$ odd and l odd (designated Class 1a) are always of comparatively very small intensity while those from planes having $h + k + l$ odd and l even (designated Class 1b) are not, and this observation holds good not only for the potassium salt but also for the ammonium and rubidium salts.

TABLE VI

PARAMETER VALUES FOR WHICH D_{hk}^{14} STRUCTURE FACTORS, S, VANISH WHEN $h = k = l$ IS ODD

Arrangement	No. of equiv. pos.	h odd, k even, l even	Parameter values	
			h odd, k odd, l odd	h even, k even, l odd
(a)	2	S always zero	S always zero	S always zero
(b)	2	S always zero	S always zero	S always zero
(c)	4	S always zero	S always zero	S always zero
(d)	4	S always zero	S always zero	S always zero
(e)	4	S always zero	S always zero	S always zero
(f)	4	$u = \frac{1}{2}$	No solution	$u = \frac{1}{2}$
(g)	4	$u = \frac{1}{2}$	No solution	$u = \frac{1}{2}$
(h)	8	S always zero	S always zero	S always zero
(i)	8	$u = 0$ or $\frac{1}{2}$;	$u = 0$ or $\frac{1}{2}$;	$u = 0, \frac{1}{2}, \frac{3}{2}$ or $\frac{5}{2}$;
		v unrestricted	v unrestricted	v unrestricted
		or $v = 0$ or $\frac{1}{2}$;	or $v = 0$ or $\frac{1}{2}$;	or $v = 0, \frac{1}{2}, \frac{3}{2}$
		u unrestricted	u unrestricted	or $\frac{5}{2}$;
(j)	8			u unrestricted
		$u = \frac{1}{2}$;	$v = \frac{1}{2}$;	$u = \frac{1}{2}$;
		v unrestricted	u unrestricted	v unrestricted
				or $v = \frac{1}{2}$;
				u unrestricted

We have given in Table VI all of the values of the parameters (exclusive of those which lead to identical arrangements or coincidence of two atoms) for which that part of the structure factor due to each of the above arrangements becomes zero whatever may be the values of h , k and l , subject to the restrictions given at the head of each column. We may, without loss of generality, place the two copper atoms at (a); the copper atoms then contribute nothing to first orders from planes with $h + k + l$ odd. The presence of such reflections shows that some of the positions (f), (g), (i) and (j) must be occupied by alkali, chlorine or water, or some combination of them. This occupancy cannot be by one kind of atom alone in any *single* arrangement except (j), for only here can a parameter value (namely, v near $\frac{1}{2}$) be found which will make reflections of Class

1a weak without making those of Class 1b weak also. No other arrangement gives a solution common to Cols. 4 and 5 but not Col. 3 of Table VI. Only the 8 chlorine atoms can occupy (j). On the other hand, if more than one of the positions (f), (g), (i) and (j) are occupied, one of these positions cannot be occupied by an alkali atom, for then weakness of reflection in Class 1a would have to be ascribed to a suitable interference between alkali and chlorine or oxygen (or both). Such destructive interference in the case of the ammonium salt could hardly remain on substitution of potassium or the much heavier rubidium. The possibility that such interference occurs between chlorine and water likewise seems remote. There remains only the possibility that the chlorine atoms are non-equivalent, four being at (f) and four at (g). With this arrangement Class 1a and not Class 1b can become weak and, in general, only when u is nearly equal to v . We conclude, therefore: (1) that the alkali atoms are at (c), (d) or (e); (2) that the chlorine atoms are either all equivalent at (j) with v near $\frac{1}{4}$, or that they are two groups of four at (f) and (g) with u nearly equal to v .

The spectral data (Tables II, III, IV) show that with all three salts the second order from (001) was much weaker than the fourth, and that the second was relatively weakest from the rubidium salt, being of almost vanishing intensity in this case. The alternative chlorine positions which remain place the chlorine atoms either [(f) and (g)] equally in basal planes with the copper atoms, or (j) in basal planes practically half way between them. Simple calculations of the basal plane structure factors for the second and fourth orders make it evident that with the chlorine at (j) the alkali atoms must be at (c) in order to make the second order of the rubidium salt reasonably weak; and that with the chlorine at (f) and (g) the alkali atoms must be at (d), or at (e) with w near $\frac{1}{4}$. These conclusions require only the approximate use of atomic numbers or electron numbers and are not markedly dependent upon the position of the water molecule. The positions (e) for the alkali atoms involves placing three positive atoms in a line in a distance of 8 Å. and placing an alkali at about 2 Å. from a copper atom; this is regarded as so improbable that it has not been treated further. We are thus left with two main alternatives: (1), 2Cu at (a), 8Cl at (j) with v near $\frac{1}{4}$, 4 alkali at (c), 4H₂O at (d), (e), (f) or (g); (2), 2Cu at (a), 4Cl at (f) and 4Cl at (g) with u nearly equal to v , 4 alkali at (d), 4H₂O at (c), (e), (f) or (g).

A piece of evidence against Arrangement (j) for a chlorine atom is the strength of the fourth order from (101) as compared with the second; in the case of the ammonium compound the fourth was practically as strong as the second, thus requiring a larger structure factor for the fourth order. Neglecting water, the structure factors given by the arrangement involving (j) are

$$n = 2 \quad S = 2\overline{Cu} + 4\overline{alk} + 8\overline{Cl} \cos 4\pi u \cos 4\pi v$$

$$n = 4 \quad S = 2\overline{Cu} + 4\overline{alk} + 8\overline{Cl} \cos 8\pi u \cos 8\pi v$$

For the values $u = \frac{1}{4}$, $v = \frac{1}{4}$, these both reduce to $2\overline{Cu} + 4\overline{alk} + 8\overline{Cl}$. The effect of changing the parameter values away from $\frac{1}{4}$ is to reduce the $8\overline{Cl}$ term for all values of u or v near $\frac{1}{4}$, and to reduce it more in the fourth than in the second order (the only values of u and v compatible with other data are sufficiently near to $\frac{1}{4}$ for this to apply). Hence, the only way in which the fourth can be made greater than the second is by water; it is regarded as doubtful whether the scattering power of water is great enough to account for the observed difference. On the other hand, the arrangement with (Cl) at (f) and (g) leads with parameter values determined below to a much larger structure factor for the fourth than for the second order even when water is omitted.

A similar piece of simple evidence comes from powder photographs of the potassium and of the ammonium salt made with molybdenum $K\alpha$ radiation in a General Electric Company cassette. The strong line due to (110) second order was stronger than that due to (101) second order occurring at a slightly smaller angle. As the number of cooperating planes for (110) is only half that for (101), the structure factor must be the greater for (110). Arguments similar to those used above again favor chlorine at (f) and (g) rather than at (j).

Other data which again eliminate (j) are the Laue photographic comparisons: (551) > (351); (151) > (241); (632) > (542). These have the disadvantage of involving only small intensity differences, but the advantage of not involving relative reflecting powers.

Finally, the alternative involving (f) and (g) as chlorine positions remains to be considered. In this case the possibility of water also being at (f) and (g) is removed by the chemical improbability of such a structure, by the necessary close approach of the chlorine and copper atoms and the water molecule, and also by the fact that planes having $h + k + l$ odd and l odd are uniformly weak no matter what the interplanar distance is.

Evaluation of the Parameters.—In order that the spectral data from (101)_s shall be satisfied, u and v must be in the region 0.18 to 0.32. The following comparisons from Photograph 2 restrict the parameters to the region (0.21, to 0.23); (418) > (652), (652) > (643), (652) > (128). This region could not be further restricted by intercomparisons not involving assumptions concerning relative reflecting powers. The near equalities of the intensities of reflections (386) \geq (4.1.10) and (652) > (128), together with the required separation of the two parameters, suggest $u = 0.213$ and $v = 0.217$, or vice versa, as the most probable values.⁶ A consideration of other data is necessary to distinguish between u and v .

⁶ The values $u = \frac{1}{4} - \beta$ and $v = \frac{1}{4} - \alpha$ lead to the same structures as the values $u = \alpha$ and $v = \beta$ and hence do not require separate consideration.

The following observed inequalities of reflections, $(473) > (471)$, $(653) > (651)$, $(387) > (385)$, between planes having $h + k + l$ even and l odd, require oxygen to be at (e), with a value of w between 0.250 to 0.333; these comparisons do not involve the assumption of numerical relative reflecting powers. A closer restriction of w can be made by comparisons affected by the value of the chlorine parameter; $(149) > (167)$, $(219) > (651)$ require w to be between 0.315 and 0.333. We have taken 0.32 as an approximate value.

TABLE VII

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CUPRIC CHLORIDE DIHYDRATE
Incident Beam 8° from normal to $(110)_s$.

hkl	d_{hkl} , Å.	$n\lambda$, Å.	Estimated intensity	S for	
				$u = 0.213$	$v = 0.217$ $w = 0.318$ 50% increase for Cu over atomic number
123	2.064	0.33	3.0	5.06	5.86
114	1.842	.40	0.80	1.24	0.44
234	1.425	.40	0.50	2.68	2.68
334	1.357	.32	0.20	1.91	2.71
433	1.295	.40	1.20	5.15	5.95
017	1.112	.36	1.0	3.58	4.38
542	1.102	.36	0.30	2.78	2.78
362	1.067	.44	1.15	6.10	6.10
217	1.066	.45	1.10	3.43	4.23
255	1.038	.40	0.38	1.40	2.20
436	0.983	.42	.65	4.85	4.85
643	.962	.45	.00		
650	.953	.34	.10	3.48	3.48
651	.947	.31	.07	2.83	3.63
128	.944	.34	.09	3.30	3.30
		.36	.10		
471	.929	.35	.08	2.67	3.47
652	.927	.35	.10	3.49	3.49
653	.896	.35	.09	5.58	6.38
527	.879	.41	.30	3.36	4.16
473	.867	.33	.10	5.42	6.22
418	.865	.36	.30	6.00	6.00
219	.847	.31	.10	4.45	5.25
167	.828	.46	.30	3.58	4.38
419	.788	.44	.37	4.50	5.30
385	.763	.38	.09	2.04	2.84
059	.756	.38	.17	4.62	5.42
386	.726	.47	.16	6.17	6.17
4.1.10	.721	.45	.16	6.00	6.00
1.5.10	.692	.41	.37	9.61	10.41
3.8.7	.689	.44	.09	4.01	4.81
1.6.10	.662	.45	.15	7.54	7.54
9.6.4	.655	.38	.02	3.12	3.12
7.3.10	.613	.43	.20	8.30	9.10

* Cl is to be taken as unity.

The only remaining undetermined factor is whether $u = 0.213$, $v = 0.217$, or the reverse. This question can be answered only by a consideration of data from all types of planes—it will depend upon relative reflecting powers as well as the usual assumptions of the methods of analysis of Laue photographs. The final tabulation of Laue data as given in Table VII, compiled from Photograph 2, shows the agreement obtained with $u = 0.213$ and $v = 0.217$. The structure factors have been calculated, first using atomic numbers and then using a reflecting power of copper increased by 50%. No data either from Laue photographs or spectral photographs were obtained in disagreement with these parameter values.

The Crystal Structure of Ammonium and Rubidium Cupric Chloride Dihydrates

The analysis of the data obtained from Laue and spectral photographs of these two compounds leads to conclusions similar to those given above. The values of the parameters were determined under the assumption that u_{Cl} and v_{Cl} did not differ by more than 0.015 (the value found in the case of potassium cupric chloride dihydrate being 0.004). The agreement between the observed intensities and calculated structure factors for spectral data is evident by reference to Tables III and IV. Table VIII gives a summary of the results obtained from the three compounds.

TABLE VIII

A SUMMARY OF PARAMETER VALUES, UNIT DISTANCES AND ATOMIC DISTANCES IN THE COMPOUNDS $R_2CuCl_4 \cdot 2H_2O$ ($R = NH_4, K$ or Rb)

Compound	$d_{100} = d_{010}, \text{\AA.}$	$d_{001}, \text{\AA.}$	u_{Cl}	v_{Cl}	w_0
$(NH_4)_2CuCl_4 \cdot 2H_2O$	7.58	7.96	0.217	0.221	0.320
$K_2CuCl_4 \cdot 2H_2O$	7.45	7.88	.213	.217	.318
$Rb_2CuCl_4 \cdot 2H_2O$	7.81	8.00	.213	.217	.330

Compound	Atomic distances, \AA.				
	Cu to nearest oxygen	Cu to nearest Cl at (f)	Cu to nearest Cl at (g)	Cu to nearest R	R to nearest Cl at (f)
$(NH_4)_2CuCl_4 \cdot 2H_2O$	2.55	2.44	3.14	4.28	3.28
$K_2CuCl_4 \cdot 2H_2O$	2.51	2.37	3.15	4.21	3.32
$Rb_2CuCl_4 \cdot 2H_2O$	2.64	2.41	3.20	4.38	3.43

Discussion of the Structure

Geometrical and Chemical Significance of the Structure.—The unit of structure containing two $R_2CuCl_4 \cdot 2H_2O$ is shown in Fig. 1. In this structure each copper atom is immediately surrounded by two oxygen atoms and four chlorine atoms, two of the chlorine atoms being at a distance different from the other two. The average copper to chlorine distance is 0.75 \AA. greater in one case than in the other (see Table VIII).

Each alkali atom is surrounded by four oxygen atoms, four copper atoms

and eight chlorine atoms. In this case, although the eight surrounding chlorine atoms are not all equivalent, they are practically equidistant from the alkali atom. The small difference in distance is necessary so that the Laue data can be satisfied (see next section). The average alkali to chlorine distance in these compounds is *ca.* 0.14 Å. greater than that of the corresponding alkali halides having the sodium chloride type of structure.

In the case of potassium chlorostannate K_3SnCl_6 ⁷ and of $NiCl_2 \cdot 6NH_3$,⁸ a group of six chlorines or ammonias is equidistantly placed around the central metal atom, the geometrical association being quite definite. Similarly in the case of the alkali cupric chloride dihydrates, each chlorine or water has one copper atom which is nearer to it than any other copper atoms are; and if the chlorine or water be regarded as associated with this copper atom, and the process repeated for all chlorine and water, the result is an array of cupric chloride dihydrate groups.

These groups are all alike and are octahedral in shape, but not regular. However, any physical unity or stability cannot be attributed to these groups on such purely geometrical grounds. Indeed, in view of the considerable inequality in the two copper to chlorine distances, it is natural to assume that the forces exerted by the copper on

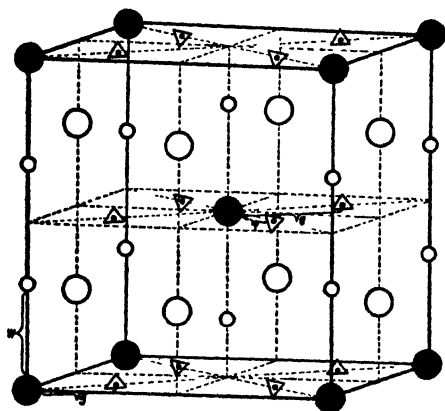


Fig. 1.—The unit of structure of the alkali cupric chloride dihydrates. ▽, Cl at (*f*); △, Cl at (*g*); ○, Cu; ●, NH_4 , K or Rb; ○, O.

the surrounding chlorine atoms are quite unequal. This inequality may well correspond to a lack of stability of the coördination group, which would be in agreement with the behavior of the substance in solution as a double salt rather than as a complex salt.

These compounds represent a new structural type. Although they have the same space-group symmetry as magnesium fluoride, they are not related to magnesium fluoride in the simple manner in which potassium chlorostannate is related to calcium fluoride.

Discussion of the Method of Analysis

In making use of absences of reflections from planes in positions to reflect, in order to determine the correct space group, it is desirable to examine combinations of special positions in the eliminated space groups

⁷ Dickinson, *THIS JOURNAL*, **44**, 276 (1922).

⁸ Wyckoff, *ibid.*, **44**, 1239 (1922).

in order to be certain that the observations could not be accounted for by giving particular values to the parameters. In the present case such a method reduces the number of space groups to two, C_{4v}^4 and D_{4h}^{14} . Since C_{4v}^4 can approximate arrangements from D_{4h}^{14} as closely as desired, we have made the *assumption* that the crystallographically assigned symmetry is correct. Such an assumption has proved to be incorrect in some cases (penta-erythritol, sodium periodate, etc.).

An observation of great value to us in the structure determination was the presence of weak reflections from planes with $h + k + l$ odd and l odd. It is conceivable that these reflections appear only because of a dissymmetry in a particular kind of atom, chlorine for instance. However, when two such planes reflected at the same wave length, and the one with the smaller interplanar distance was the more intense, its structure factor, with a separation of the value of u and v not exceeding (0.03) in case of chlorine (f) and (g), was always found to be the greater of the two. This is of further interest since arrangements with chlorine at (j) could not account for such an observation.

The elimination of the arrangement with chlorine at (j) is not as straightforward as one might wish. It is based upon rather close Laue comparisons, and a general disagreement with the spectral data. Reflections for which chlorine at (j) and at (f) and (g) would lead to considerably different intensities require some knowledge of reflecting powers in their treatment.

The determination of the chlorine parameters has been made independently of relative reflecting powers; but our determination of which value represents u and which v is not a very good one. The difference between the two is, however, very small.

It is not probable that oxygen reflects strongly enough to be a factor governing markedly the intensity of the Laue spots. Small intensity differences in our data require a parameter for oxygen, however. The parameter determination in the case of oxygen at (e) is of approximate character only. The data, without assumptions concerning relative reflecting powers, could not be explained by placing oxygen at (c) or (d). This elimination of (c) and (d) is based on several comparisons, all of which are necessarily close.

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Summary

The structures of crystals of ammonium, potassium and rubidium cupric chloride dihydrates have been investigated by means of Laue and spectral photographs interpreted with the aid of the theory of space groups. The unit of structure, based on a simple tetragonal lattice,

contains two $R_2CuCl_4 \cdot 2H_2O$. The space-group symmetry is probably D_{4h}^{14} with 2Cu at (a), 4 alkali at (d), 4Cl at (f), 4Cl at (g) and $4H_2O$ at (e). The compounds seem to have "double salt" characteristics.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE CONDUCTIVITY OF ACIDS AND SALTS IN LIQUID AMMONIA¹

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In the course of the development of the system of compounds derived from liquid ammonia as a solvent, by Franklin² and his associates, it was desired to know the extent to which certain acids and salts would ionize when dissolved in liquid ammonia. This information was designed to indicate whether or not metallic salts of acids derived from the ammonia system, when dissolved in liquid ammonia, would ionize to a greater extent than their respective acids. This conspicuous property of salts of aquo-acids in water solution would thus serve to test the validity of the classification of the former as true salts.

Also it was hoped that such information would be a useful addition to existing knowledge of the properties of substances dissolved in liquid ammonia.

Some of the data obtained by Franklin³ and by Franklin and Kraus⁴ are made use of for purposes of comparison.

Treatment and Expression of Results

The following notation has been used to express the designated quantities: R , measured resistance; C , cell constant; v , dilution, in liters per mole; Λ , molecular conductivity; Λ_∞ , the value approached by Λ as the dilution increases; K , the ionization or equilibrium constant.

The conductivity curves of the substances measured, with some of the curves of Franklin and of Franklin and Kraus, have been plotted together in Fig. 1 for comparison.

The graphical methods of Kraus and Bray⁵ have been used, where applicable, to evaluate Λ_∞ and K , and these values are given in Tables I and II.

¹ From a thesis presented to the Department of Chemistry and the Committee on Graduate Study of Stanford University in 1925 in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work herein described was done under the direction of Dr. E. C. Franklin.

² Franklin, "Liquid Ammonia as a Solvent," A. C. S. Monograph in preparation.

³ Franklin, *Z. physik. Chem.*, **69**, 270 (1909).

⁴ (a) Franklin and Kraus, *Am. Chem. Jour.*, **23**, 277 (1900); (b) *THIS JOURNAL*, **27**, 191 (1905).

⁵ Kraus and Bray, *THIS JOURNAL*, **35**, 1315 (1913).

Experimental

The measurements were made at -33.5° , using cells described by Elsey,⁶ and technique which differs only in certain details from that described by him, or by Franklin and Kraus.^{4a}

The cell constants were redetermined, using 0.02 *M* potassium chloride at 20 and at 0° , and 0.01 *M* potassium chloride at 18° , prepared by the method of Kraus and Parker,⁷ and using the values for the specific conductivity given by Kohlrausch and Holborn,⁸ and by Kraus and Parker, respectively.

The resistance measurements were made by comparison with a standard 1-100,000 ohm box of Curtis coils, by means of a Kohlrausch drum slide wire, both made by Leeds and Northrup, and used by Elsey.

The alternating current was obtained from a micro-hummer giving a sine wave current with a frequency of 1000.

The telephone current was amplified by means of a device described by Hall and Adams.⁹

The entire apparatus was shielded with grounded metal. The wires leading from the cell vessel were No. 18 double cotton covered copper, enclosed in separate grounded lead tubes. These wires under operating conditions had a resistance of 0.16 ohm, which was deducted from all resistance measurements.

Satisfactorily sharp minima were obtained by the use of capacity in parallel with the resistance box.

For reasons set forth in the following paper, the resistance measurements herein described were made by means of the concentric pair of electrodes only.

A measured volume of a solution of determined concentration and resistance was diluted with successive measured portions of pure solvent, distilled from the reservoir and condensed directly in the conductivity cell. The new concentration was calculated, and the new resistance measured, after each dilution.

All results have been corrected by subtracting the specific conductivity of the solvent, as obtained before and after each series of measurements, from that of the solution.

The specific conductivity of the solvent was usually from 0.1 to 0.2×10^{-6} mhos.

Preparation of Materials

The substances used in making these measurements have been obtained from several sources. Two were Kahlbaum preparations, ten were

⁶ Elsey, *THIS JOURNAL*, **42**, 2454 (1920).

⁷ Kraus and Parker, *THIS JOURNAL*, **44**, 2422 (1922).

⁸ Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," B. G. Teubner, Leipzig, 1916.

⁹ Hall and Adams, *THIS JOURNAL*, **41**, 1515 (1919).

prepared or purified by the writer, and ten were prepared and purified by other workers, notably W. L. Burdick, J. S. Blair and F. W. Bergstrom, to whom thanks are due. In cases of uncertainty the purity has been verified by analysis and, with the exception of dicyanodiamide and melamine, the purity of all are within the limits of the experimental error of the measurements.

Results

The molecular conductivity at $\log v = 3.0$ of seven acids and their respective alkali-metal salts is shown in Table I.

TABLE I
THE CONDUCTIVITY OF ACID AND SALT COMPARED

Electrolyte	Formula	$\Delta_{\log v = 3.0}$	$10^4 K$	
I. Potassium <i>m</i> -nitrobenzene-sulfonamide	$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NHK}$	201	275	15.0
II. <i>m</i> -Nitrobenzenesulfonamide	$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2$	162	231	12.5
4. Potassium succinimide	$\text{CH}_2\cdot\text{CO}:\text{NK}$ $\text{CH}_2\cdot\text{CO}:\text{NK}$	135	298	3.03
3. Succinimide	$\text{CH}_2\cdot\text{CO}:\text{NH}$ $\text{CH}_2\cdot\text{CO}:\text{NH}$	138	286	2.45
7. Monosodium cyanamide	$\text{NC}\cdot\text{NHNa}$	205		
III. 5. Cyanamide	$\text{NC}\cdot\text{NH}_2$	35		
16. Dipotassium α -triphenyl-guanidine	$\text{C}_6\text{H}_5\text{N}:\text{C}(\text{KNC}_6\text{H}_5)_2$	154		
6. α -Triphenylguanidine	$\text{C}_6\text{H}_5\text{N}:\text{C}(\text{HNC}_6\text{H}_5)_2$	0.75		
14. Potassium <i>isobutyramide</i>	$(\text{CH}_3)_2\text{CH}\cdot\text{CONHK}$	126	290	2 ± 0.2
10. <i>Isobutyramide</i>	$(\text{CH}_3)_2\text{CH}\cdot\text{CONH}_2$	0.025		
15. Potassium valeramide	$\text{C}_4\text{H}_9\cdot\text{CONHK}$	123	287	1.8
11. Valeramide	$\text{C}_4\text{H}_9\cdot\text{CONH}_2$	0.5		
22. Potassium acetamide	CH_3CONHK	155	328	1.8
V. Acetamide	CH_3CONH_2	0.9		

TABLE II
THE CONDUCTIVITY OF OTHER ACIDS AND SALTS

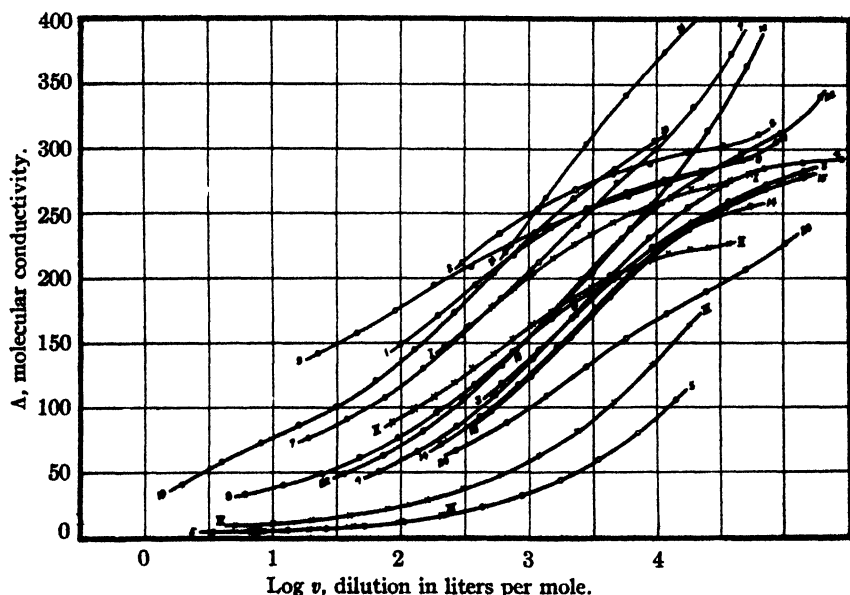
Electrolyte	Formula	$\Delta_{\log v = 3.0}$	Δ_∞	$10^4 K$
1. Ammonium azide	NH_4N_3	227	291.5	15.0
2. Sodium dicyanamide	$\text{NaN}(\text{CN})_2$	249	305 ± 3	17 ± 3
8. Monosodium ammono-aluminate	$\text{NaAl}(\text{NH}_2)_4$	155	227	14.0
9. Sulfur nitride	S_4N_4	233	298	0.8
19. Sodium cyanide	NaCN	230	349 ± 2	0.88
12. <i>o</i> -Nitrobenzamide	$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$	2
13. <i>p</i> -Nitrobenzamide	$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$	0.5
17. Dicyanodiamide	$(\text{NC}\cdot\text{NH}_2)_2$	0.7
18. Melamine	$(\text{NC}\cdot\text{NH}_2)_3$	0.8
20. Trisodium tricyanomelamine	$[\text{NaN}(\text{CN})_2]_3$	100
21. Tripotassium hydromelionate	$\text{K}_3\text{C}_9\text{N}_{13}$	244

Values of Λ at this same dilution for other acids and salts are given in Table II.

The dilution $\log v = 3.0$ was chosen because the values of Λ are perhaps better distributed in this region than in any other which includes as many curves.

Values of Λ_∞ and K could not be determined by the graphical method of Kraus and Bray with substances not binary electrolytes; and the use of this method with binary electrolytes of very low conductivity leads to unreasonably low values for Λ_∞ , with correspondingly high values for the degree of dissociation and for K . Therefore, no attempt has been made to assign values to those substances.

The number assigned to a substance in the tables is the same as that which designates the curve for that substance in Fig. 1. The Roman numerals refer to substances measured by Franklin and Kraus.



X—Franklin and Kraus: I, Potassium *m*-nitrobenzenesulfonamide; II, *m*-Nitrobenzenesulfonamide; III, Mercury succinimide; IV, Cyanamide. O—Smith: 1, Ammonium azide; 2, Sodium dicyanamide; 3, Succinimide; 4, Potassium succinimide; 5, Cyanamide; 7, Monosodium cyanamide; 8, Monosodium ammonio-aluminate; 9, Sulfur nitride; 14, Potassium *isobutyramide*; 15, Potassium valeramide; 16, Dipotassium α -triphenylguanidine; 19, Sodium cyanide; 20, Trisodium tricyanomelamine; 21, Tripotassium hydromelonate; 22, Potassium acetamide.

Fig. 1.—The conductivity of acids and salts in liquid ammonia.

Discussion

On account of several considerations treated in the following paper, and because with many of the substances it is difficult to attain and main-

tain any considerable degree of purity, no great accuracy can be claimed for the results presented above. However, the least accurate of them is probably not in error by more than 5%.

It is immediately evident from Fig. 1 that only a few of the curves correspond more than approximately to the dilution law of Kraus and Bray.⁵ Obviously many of the substances do not behave as simple binary electrolytes.

A point of inflection at about $\log v = 4.5$ seems to be common to most of the curves in Fig. 1, at which point the slope again increases.

The curves as a group approach a value just under 300 for Λ_{∞} . The fact that in certain cases curves of nearly ideal form were obtained, serves as a check upon the manipulation as well as upon the accuracy with which the dilutions could be made.

The curves of the acid amides, the polymers of cyanamide and α -triphenylguanidine have not been plotted in Fig. 1 because of the extremely small values of Λ involved.

One might expect the acid amides to be poor conductors, since they are analogs of the weak carboxylic acids. Although they are formally dibasic acids, only one hydrogen atom can be replaced by potassium in liquid ammonia solution, and it is probable that the ionization of the second is immeasurably small. This is in harmony with the fact that their salts behave essentially as binary electrolytes.

As may be seen from Table I, the salt is in every case but one a better conductor than the corresponding acid. The difference, however, is small in case the acid is one of the so-called "strong" acids. Possibly since the "strong" acid is capable of forming a stable ammonium salt, it does so, and the conductivity measured is that of the ammonium salt. Succinimide, for example, is stable and has weak acid properties in water solution.

The mercury salt of succinimide (Fig. 1) runs true to the form of mercury salts in general, exhibiting a very low conductivity, as compared with most salts, in liquid ammonia, as in water.

In considering the ammonio-carbonic acids,¹⁰ it is interesting to note that the conductivity of both acids and salts, in so far as it has been measured, increases with de-ammonation of the acids, and decreases with polymerization. The most completely ammonated acid, and the more polymerized acids, are very poor conductors, while the monomolecular de-ammonation product, $\text{HN}(\text{CN})_2$, is a strong acid even in water solution. This is in harmony with results reported by Madelung and Kern,¹¹ who show that dicyanimide, $\text{HN}(\text{CN})_2$, is a strong acid in water solution, and that the triamer, tricyanomelamine, is a somewhat weaker

¹⁰ Franklin, *THIS JOURNAL*, **44**, 486 (1922).

¹¹ Madelung and Kern, *Ann.*, **427**, 1 (1922).

one in practically the same ratio that has been found by the writer for the conductivity of their respective salts in liquid ammonia solution.

Sulfur nitride is noteworthy for the reason that it is a good conductor, and that the form of the curve is that of a binary electrolyte. Sulfur nitride has been shown¹² to be a mixed anammonide of ammonio-sulfurous, and ammonio-thiosulfuric acids. The possibility of ammonation, with the resulting formation of the above acids, is precluded by the small slope of the curve, and the absence of insoluble material. It is suggested that the substance dissociates into the two anammonous radicals which on ammonation would give the respective acids.

In conclusion, the writer wishes to express the most sincere thanks to Dr. E. C. Franklin for assistance, suggestions and advice which always have been readily available.

Summary

Conductivity measurements have been made in liquid ammonia solution at -33.5° on twenty-two substances.

In every case but one, the alkali metal salt of an acid proved to be a much better conductor than the acid itself.

The acid amides are very poor conductors, while their alkali metal salts are good conductors and behave as binary electrolytes.

The conductivity of the ammonio-carbonic acids, and their alkali metal salts, increases with de-ammonation of the acid, and decreases with polymerization.

The graphical method of Kraus and Bray has been used to evaluate Λ_{∞} and K , for twelve substances.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

A SOURCE OF ERROR IN CONDUCTIVITY MEASUREMENTS¹

By FRANCIS A. SMITH

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In studying the literature on the measurement of electrolytic conductivity, one meets with statements of conclusions such as those of Washburn,² and of Schlesinger and Read.³

The former states, in substance, that a cell should be designed, in resistance capacity, for the particular solution the resistance of which is to be measured in it; and that only solutions having resistances varying

¹² Unpublished observations made in this Laboratory.

¹ See preceding paper. Since this paper was first prepared, a paper by Randall and Scott, *THIS JOURNAL*, 49, 636 (1927), has appeared which presents similar results.

² Washburn, *THIS JOURNAL*, 38, 2431 (1916).

³ Schlesinger and Read, *ibid.*, 41, 1727 (1919).

within rather narrow limits are suited for use with a cell having that particular resistance capacity.

The latter show that the value of the cell constant depends upon the resistance of the solution by means of which it is determined, and should be known for all resistances within the range of the measurements for which the cell is to be used.

The use by the writer⁴ of a conductivity cell containing three electrodes provided a striking corroboration of the above conclusions, probably on account of the design of the cell and the method of making the measurements. The electrodes consisted of three co-axial cylinders open at the

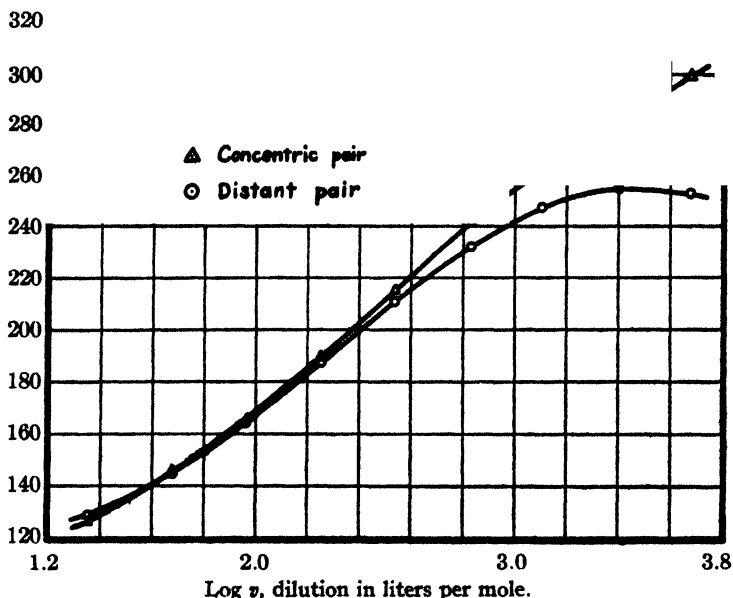


Fig. 1.—Conductivity curves of NH_4NO_3 in liquid NH_3 , resulting from measurements of resistances of two cells formed by three electrodes in the same solution.

ends, two of which were concentric and close together, and the third, at some distance from the others, presented its edge to the edges of the others.

The measurements were made by diluting a measured volume of a solution of known concentration and resistance with successive measured portions of pure solvent, calculating the new concentration, and measuring the new resistance after each dilution.

Fig. 1 shows the ordinary conductivity curves of ammonium nitrate in liquid ammonia solution. The values of Λ for one of the curves were calculated from the measured resistances of the cell formed by the con-

⁴ See preceding paper.

centric pair of electrodes, and the values for the other curve, from the distant pair of electrodes, using the corresponding cell constants, determined as described in the preceding paper.

It is evident that as the resistance changes there is a change not only in the cell constants, but also in the ratio which they bear to one another, and that the values of Λ determined from the two cells are concordant only in that region of concentration and resistance in which the 0.02 *M* and 0.01 *M* potassium chloride solutions used to determine the cell constants also fall.

The intersection of the two curves (Fig. 1) occurs at a concentration near 0.02 *M*, and the resistances of the concentric and distant cells at the near-by plotted points were 17.73 ohms, and 3574 ohms, respectively.

The resistances of the same cells containing aqueous potassium chloride are set forth in Table I.

TABLE I

THE RESISTANCES AND RESISTANCE RATIOS OF THE CELLS CONTAINING THE AQUEOUS POTASSIUM CHLORIDE SOLUTIONS WITH WHICH THE CELL CONSTANTS WERE DETERMINED

KCl aq.	Concentric cell		Distant cell	
	<i>R</i> (ohms)	<i>R</i> _{0.01 M} / <i>R</i> _{0.02 M}	<i>R</i> (ohms)	<i>R</i> _{0.01 M} / <i>R</i> _{0.02 M}
0.01 <i>M</i>	43.80		8860	
		2.033		2.033
0.02 <i>M</i>	21.55		4357	

It is seen that the ratio of the resistances of these two solutions is the same for both cells. Thus the criterion of reliability imposed by Taylor and Acree⁵ is complied with by these cells, notwithstanding their demonstrated unreliability, when used with solutions the resistances of which vary greatly from those of the potassium chloride solutions referred to in Table I.

In Fig. 2, values of the ratio of the resistance measured by means of the distant pair of electrodes to that measured by means of the concentric pair, are plotted against values of the logarithm of the resistance of the distant pair. The data were obtained from solutions of ammonium nitrate, and ammonium chloride, in liquid ammonia, and of potassium chloride in water.

It is evident that the resistance measured between the distant pair of electrodes increases more and more rapidly than that measured between the concentric pair, until the limiting resistance of the former is reached.

It had previously been found that when the walls of the cell vessel were wet with either water or ammonia, the order of magnitude of the resistance measured between either pair of electrodes never exceeded 10⁶ ohms. Consequently, on diluting a solution, as the resistance meas-

⁵ Taylor and Acree, *THIS JOURNAL*, **38**, 2409 (1916).

ured between the distant pair of electrodes reaches this maximum value, any further dilution causes a sharp decrease in the ratio of the resistances of the two cells. This condition is evidenced in Fig. 2 by the break at *m*.

It might be expected that the ratio of the resistances of the two cells would be constant, if the various factors such as effective electrode area and effective distance between electrodes remain constant. Evidently this is not the case.

The conditions assumed by Washburn² as a basis for the design of conductivity cells are, among others, plane parallel electrodes having a relatively large surface area, and separated by a relatively small distance. These conditions obviously are not fulfilled in the case of the cell formed by the distant pair of electrodes arranged edge to edge.

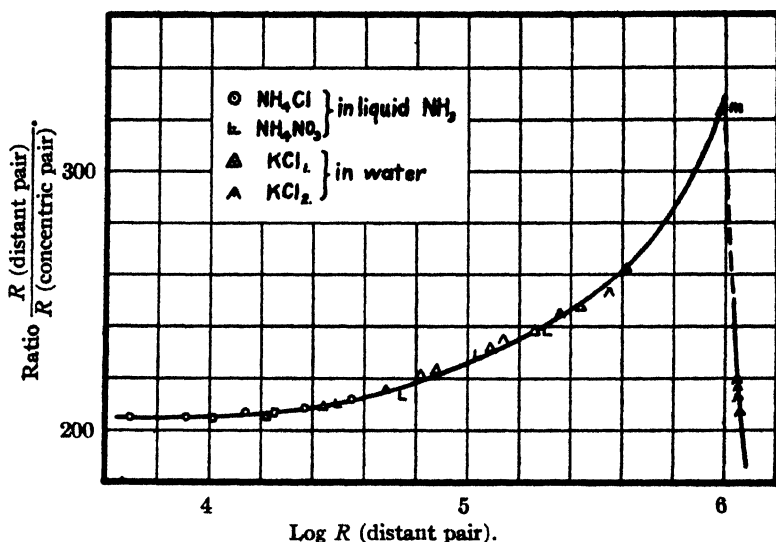


Fig. 2.—The effect of dilution on the ratio of the resistances of two cells formed by three electrodes in the same solution.

Obviously, unless the cell constant has been evaluated by means of suitably prepared solutions of known specific conductivity, which have resistances up to the highest value to be measured with the cell, all measurements made over a considerable range of resistances with a single cell are in error because the cell constant changes with resistance.

Especially liable to such error are such measurements as have been made by Franklin and Kraus,⁶ and by Franklin,⁷ Elsey,⁸ the writer⁴ and others, over a wide range of resistances by the process of dilution.

In this type of work it was the usual procedure to change from the

⁶ Franklin and Kraus, *Am. Chem. J.*, 23, 277 (1900).

⁷ Franklin, *Z. physik. Chem.*, 69, 272 (1909).

⁸ Elsey, *THIS JOURNAL*, 42, 2454 (1920).

distant pair to the concentric pair of electrodes as soon as the resistance measured between the latter exceeded 100 ohms, in order to minimize the heating effect of the current at low resistances. So long as this procedure was followed, no discrepancy became apparent, since the change was made in the region in which the corresponding values of Λ were concordant.

Elsey⁹ states that in case the change was made to the concentric pair of electrodes when their resistance was below 100 ohms, the heating effect of the current was noticeable, and that below 75 ohms there was a marked discrepancy between the corresponding values of Λ obtained from the two pairs of electrodes.

This discrepancy is indicated in Fig. 1 by the divergence of the curves for ammonium nitrate below their point of intersection, and is bound up with a shift in the bridge setting due to polarization, treated by Washburn,⁹ rather than with the heating effect of the current, or a changing cell constant. A rising temperature would produce a change in the direction opposite to that of the error indicated. The effect of a changing cell constant in this region is undoubtedly negligibly small. The shift in the bridge setting resulting when capacity is used to sharpen the telephone minimum which had been rendered indeterminate by polarization in a concentrated solution, most marked in "set-up B,"¹⁰ was in the direction of increasing resistance or decreasing values of Λ , and is probably the source of the discrepancy noted by Elsey.

Summary

The writer offers data in support of conclusions of Washburn and of Schlesinger and Read, showing that the use of a conductivity cell should be restricted to solutions having resistances of the same order of magnitude as those of the solutions used to determine the cell constant, on account of the fact that the cell constant changes with the resistance of the solution measured.

The effect of doubling the resistance of the solution between the concentric pair of electrodes of a three electrode cell was to slightly more than double the resistance of the solution between one of the concentric pair and the distant electrode. This effect amounted to about 5% at a dilution of one thousand liters per mole, and increased with dilution up to the highest resistance that could be measured between the distant pair of electrodes.

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⁹ Ref. 2, p. 2458.

¹⁰ (a) Ref. 3. (b) The usual bridge set-up with the alternating current connected to the ends of the slide wire.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A COMPUTATION OF THE FREE ENERGY AND FUGACITY IN GASEOUS MIXTURES OF ETHYLENE AND ARGON

BY G. E. GIBSON AND BENJAMIN SOSNICK

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Introduction and Discussion of Results

The determination of the fugacity or free energy of a gas in a mixture is of considerable practical and theoretical interest. Lewis and Randall¹ consider it likely that almost any gaseous solution would be nearly perfect, that is, at a given temperature and total pressure the fugacity of any constituent would be proportional to its mole fraction or partial pressure.²

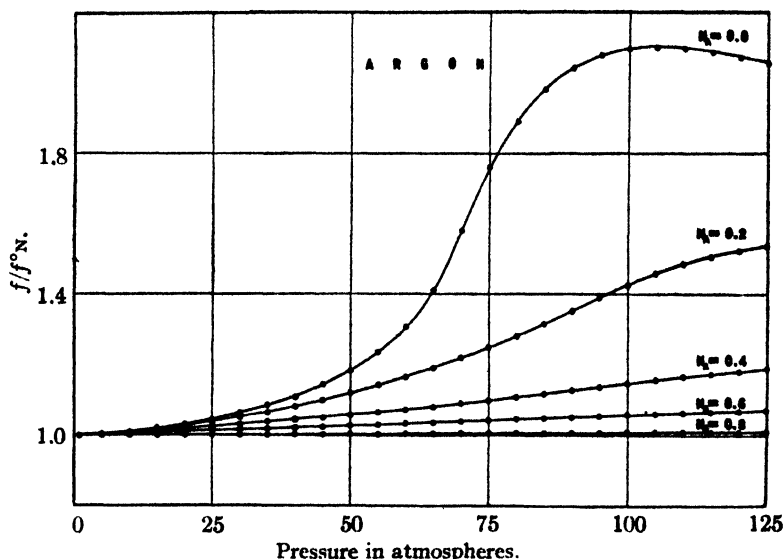


Fig. 1.—Deviation of argon in ethylene-argon mixtures from the rule of Lewis and Randall.

The partial pressure here is defined as the product of the mole fraction and the total pressure. The only data available in the literature for an accurate calculation of the fugacities in a gaseous mixture are those of Masson and Dolley,³ who determined the isotherms of gaseous mixtures of varying composition of argon and ethylene at pressures from 30 to 125 atmospheres

¹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

² In a recent article by Lurie and Gillespie [THIS JOURNAL, 49, 1154 (1927)] this rule is found to hold fairly well for the Haber equilibrium at pressures up to about 13 atm. The deviations from Dalton's law are too small, however, at these pressures for an adequate test of the rule.

³ Masson and Dolley, *Proc. Roy. Soc. (London)*, 103A, 524 (1923).

at 24.95° . The fugacities of both constituents have been calculated from these data and the results are shown graphically in Figs. 1 and 2. Details of the calculation will be given in the next section. In Fig. 1 (2) the ratios of $f/f^\circ N$ for argon (ethylene) are plotted as ordinates for various mole fractions, against the pressure in atmospheres as abscissas. Here f is the fugacity of the component under consideration, f° the fugacity of the pure component at the pressure of the mixture and N its mole fraction. The graphs show clearly the deviations of these mixtures from the perfect solution represented by the horizontal line $f/f^\circ N = 1$. In the limiting case, that of argon at zero concentration and about 100 atmospheres, the fugacity is nearly twice the value calculated on the assumption of a per-

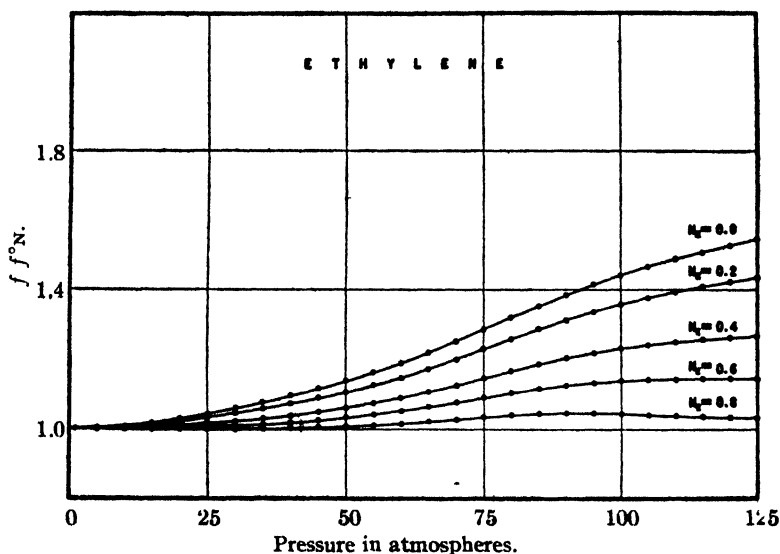


Fig. 2.--Deviations of ethylene in ethylene-argon mixtures from the rule of Lewis and Randall.

fect solution. Thus the error made in calculating the partial molal free energy on the assumption of a perfect solution is given by the difference $RT \ln f - RT \ln f^\circ N$, which in this extreme case for argon is about 440 calories. Up to about 50 atmospheres the rule of Lewis and Randall is very closely obeyed, the maximum deviation for argon at zero concentration at this pressure being about 96 calories.

Theory of the Calculation of the Fugacities from the Isotherms of Binary Mixtures

Consider a system consisting of n_1 moles of component I and n_2 moles of component II. Let its volume at total pressure P and absolute temperature T be V . The partial molal volume, \bar{v}_1 , of constituent I is defined by the equation

$$\bar{v}_1 = \frac{\partial V}{\partial n_1} \quad (1)$$

and similarly for \bar{v}_2 . The change in free energy in removing one mole of constituent I from a mixture at pressure P to a mixture of the same concentration at pressure P' is given by

$$\Delta F = \int_P^{P'} V dP \quad (2)$$

The ratio of the fugacities is then given by the equation

$$\ln \frac{f'}{f} = \frac{\Delta F}{RT} = \frac{1}{RT} \int_P^{P'} \bar{v} dP \quad (3)$$

The arbitrary constant in the fugacity is determined by making the fugacity of a perfect gas equal to its pressure. From these equations it is possible to calculate the fugacity of the constituents, when the total volume is known as a function of pressure and composition. Equation 3 is, however, not of convenient form for actual computation, and for this purpose may be transformed as follows. Defining the quantity α by the equation

$$\alpha = \frac{RT}{P} - \bar{v} \quad (4)$$

and noting that at zero pressure $f = NP$, we obtain by substitution

$$RT \ln f = RT \ln NP - \int_0^P \alpha dP \quad (5)$$

or substituting base ten logarithms for natural logarithms, we obtain with $R = 82.07$ cc. atmos. per degree

$$\log f = \log NP - \frac{1}{189.0T} \int_0^P \alpha dP \quad (6)$$

In Equation 6, f and P are expressed in atmospheres and α in cubic centimeters. In order to obtain α we must first calculate \bar{v} , and here again the basic equation, Equation 1, is not in a convenient form for computation. We have, therefore, made use of the method described in the note of Sosnick.⁴ For partial molal volumes, Sosnick's equation becomes

$$\bar{v}_1 = v_1 + \Delta + N_2 \frac{d\Delta}{dN_1}, \quad (7)$$

where v_1 is the molal volume of pure constituent I and Δ is defined by the equation

$$\Delta = v - (N_1 v_1 + N_2 v_2) \quad (8)$$

where $v = V/(n_1 + n_2)$ is the molal volume of the mixture and v_1 and v_2 are the molal volumes of the pure constituents.

The calculation thus resolves itself into the computation of N_1 , N_2 , v_1 , v_2 and v from the data of Masson and Dolley,³ the graphical evaluation of \bar{v}_1 and \bar{v}_2 , using Equations 7 and 8, and the evaluation of the fugacity by graphical integration, using Equations 4 and 6.

⁴ Sosnick, Note, THIS JOURNAL, 49, 2255 (1927).

Calculation of the Fugacities in the Mixtures of Ethylene and Argon From the Data of Masson and Dolley

Masson and Dolley³ express their results in terms of "density D " which they define by

$$D = \frac{\text{sum of separate volumes at 1 atm.}}{\text{volume of mixture at } P \text{ atm.}} \quad (9)$$

The composition is expressed as percentage by volume of the separate constituents at one atmosphere. In order to calculate the mole fraction N from the volume per cent. V.P. we first obtain the molal volumes v_1 and v_2 of argon and ethylene, respectively, from the liter weight L of these gases, namely, $L_A = 1.781$ g. per liter at 0° and 1 atm.⁵ and $L_{C_2H_4} = 1.2609$ g. per liter at 0° and 1 atm.,⁶ and then employ the equations

$$N_1 = 1 - N_2 = (V.P.)_1/v_1 / \left(\frac{(V.P.)_1}{v_1} + \frac{100 - (V.P.)_1}{v_2} \right) \quad (10)$$

The molal volumes, v , of the mixture are now obtained from the equation

$$v = \frac{N_1 v_1 + N_2 v_2}{D} \quad (11)$$

and are given in Table I.

TABLE I
MOLAL VOLUMES

P (atmos.)	0.0000	0.2490	0.5017	0.6007	0.7091	0.9014	1.0000
1	24478	24425	24371	24350	24327	24286	24265
5	4882						4729
10	2431						2291
15	1615						1477
20	1208						1070
25	962.6						824.5
30	800.2	781.6	749.0	738.1	721.4	681.2	658.7
35	684.3	665.5	636.3	621.65	607.9	563.2	538.3
40	597.0	578.5	549.3	534.5	517.5	474.15	446.7
45	529.5	511.0	481.8	466.8	449.2	403.9	374.2
50	475.6	457.1	427.6	412.7	394.6	347.4	313.8
55	431.3	413.1	383.8	368.7	349.9	300.3	262.5
60	394.6	376.6	347.3	332.0	312.5	260.3	216.75
65	363.5	345.6	316.5	300.9	280.9	226.3	174.8
70	336.8	319.2	290.1	274.4	251.7	197.1	141.3
75	313.9	296.3	267.4	251.55	230.7	171.9	118.6
80	293.9	276.2	247.6	231.7	210.9	151.0	105.9
85	276.1	258.8	230.2	214.35	193.5	134.55	98.36
90	260.4	243.2	214.8	199.3	178.2	122.1	93.435
95	246.4	229.2	201.2	185.45	165.0	112.6	90.00
100	233.8	216.9	189.1	173.4	153.5	105.5	87.25
105	222.4	205.8	178.2	162.9	143.4	100.1	85.02
110	212.1	195.7	168.5	153.6	134.7	95.92	83.24

⁵ Watson, *J. Chem. Soc.*, 97, 533 (1910).

⁶ Stahrfoss, *Arch. sc. phys.*, 23, 304 (1908).

TABLE I (Concluded)

P (atmos.)	-Mole fractions of C_6H_6 -					
	0.0000	0.2490	0.5017	0.6007	0.7091	0.9014 1.0000
115	202.7	186.6	159.8	145.4	127.1	92.52 81.76
120	194.1	178.3	152.0	137.9	120.7	89.68 80.375
125	186.3	170.6	145.0	131.3	115.2	87.30 79.22

The partial molal volumes calculated from Equation 7 are given in Table II.

TABLE II
PARTIAL MOLAL VOLUMES

P (atmos.)	Mole fractions of $C_6H_6(N_2)$											
	0.0	0.2	0.4	0.6	0.8	1.0						
	\bar{v}_1	\bar{v}_2	\bar{v}_1	\bar{v}_2	\bar{v}_1	\bar{v}_2	\bar{v}_1	\bar{v}_2	\bar{v}_1	\bar{v}_2	\bar{v}_1	\bar{v}_2
1	24478											24265
5	4882											4729
10	2431											2291
15	1615											1477
20	1208											1070
25	962.6											824.5
30	800.2	735.1	802.8	718.4	814.0	692.5	829.6	677.2	863.5	662.2	888.6	658.7
35	684.3	619.9	687.1	601.2	697.8	576.7	716.2	558.9	752.3	544.0	797.7	538.3
40	597.0	534.3	600.6	512.3	610.6	489.3	626.0	474.9	678.5	453.7	724.1	446.7
45	529.5	465.4	532.0	447.9	542.9	422.8	559.4	405.7	616.0	383.6	676.2	374.2
50	475.6	412.0	478.8	391.6	489.0	367.8	506.1	351.6	565.4	327.1	667.6	313.8
55	431.3	368.4	433.9	351.5	445.4	324.4	465.2	304.8	528.6	279.9	669.9	262.5
60	394.6	332.0	397.0	316.2	409.3	288.0	432.8	264.9	498.9	238.9	707.1	216.8
65	363.5	298.4	365.7	285.2	378.7	256.7	401.1	234.4	474.8	205.4	801.5	174.8
70	336.8	273.9	339.1	259.4	353.0	229.7	383.4	201.2	447.1	174.5	996.8	141.3
75	313.9	249.8	316.3	236.1	328.9	208.8	354.8	182.7	435.6	161.2	726.9	118.6
80	293.9	229.8	296.2	215.9	307.8	190.6	335.9	162.5	424.7	128.7	576.9	105.9
85	276.1	214.8	278.3	200.2	290.7	173.0	319.2	144.6	411.2	109.5	456.1	98.4
90	260.4	201.2	262.8	184.8	274.8	157.7	302.8	130.3	395.6	94.2	372.4	93.4
95	246.4	187.3	248.6	171.7	260.7	144.5	288.3	117.1	376.9	82.8	306.4	90.0
100	233.8	173.6	235.6	161.0	248.3	133.3	274.0	106.5	354.9	75.0	256.8	87.3
105	222.4	162.3	224.4	149.6	237.1	122.1	262.3	96.8	321.1	72.2	222.4	85.0
110	212.1	154.3	214.2	140.3	226.1	113.5	250.0	89.5	290.6	71.2	192.3	83.2
115	202.7	145.5	205.1	131.0	216.4	105.8	239.3	83.0	264.3	70.9	172.7	81.8
120	194.1	138.8	196.4	124.4	207.8	98.5	227.7	78.1	243.1	70.2	158.4	80.4
125	186.3	130.6	188.1	118.9	199.2	93.4	216.5	74.5	223.8	69.9	144.7	79.2

From Table II the values of $\alpha = RT/P - \bar{v}$ (Equation 4) were calculated and are plotted against P for various mole fractions in Fig. 3. The values of $\int_0^P \alpha dP$ were obtained by graphical integration of these curves, and thence by Equation 9 the values of $\log f$ from which the curves of f/f^N plotted in Figs. 1 and 2 were derived. The free energies given in Tables III and IV were obtained by multiplying the values of $\log f$ by $1364.9 = (2.3026RT)$.

TABLE III
FREE ENERGY OF ARGON

P (atmos.)	N_2 in C_6H_6				
	0.0	0.2	0.4	0.6	0.8
1	0	-132	-302	-543	-954
5	954	822	652	412	2

TABLE III (Concluded)

P (atmos.)	$\% \text{C}_2\text{H}_6$				
	0.0	0.2	0.4	0.6	0.8
10	1364	1231	1063	825	415
15	1602	1470	1304	1067	658
20	1771	1639	1474	1239	832
25	1901	1769	1606	1372	969
30	2007	1876	1714	1482	1082
35	2097	1966	1805	1575	1180
40	2174	2043	1884	1656	1266
45	2242	2112	1953	1728	1344
50	2303	2173	2016	1793	1416
55	2358	2228	2072	1851	1482
60	2408	2278	2124	1906	1544
65	2454	2325	2172	1956	1603
70	2496	2367	2216	2004	1659
75	2535	2407	2257	2048	1713
80	2572	2444	2296	2090	1765
85	2607	2479	2332	2130	1816
90	2639	2511	2366	2167	1865
95	2670	2542	2399	2203	1911
100	2699	2572	2430	2237	1956
105	2727	2600	2459	2270	1997
110	2753	2626	2487	2301	2034
115	2778	2652	2514	2330	2067
120	2802	2676	2540	2359	2098
125	2825	2699	2564	2386	2126

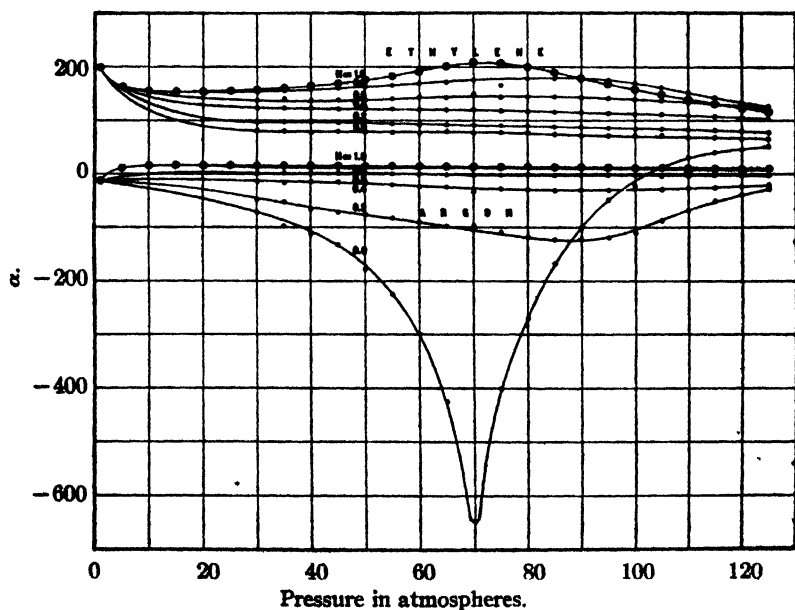
Fig. 3.—Graph of α as a function of P .

TABLE IV
 FREE ENERGY OF ETHYLENE

$P(\text{atmos.})$	$\text{M}_{\text{C}_2\text{H}_4}$				
	0.2	0.4	0.6	0.8	1.0
1	-959	-548	-308	-137	-5
5	-22	389	629	799	932
10	373	781	1021	1191	1323
15	599	1005	1243	1413	1545
20	756	1160	1396	1565	1697
25	876	1277	1511	1679	1810
30	972	1370	1603	1768	1899
35	1052	1446	1677	1841	1972
40	1119	1511	1740	1901	2031
45	1177	1566	1793	1952	2081
50	1228	1614	1838	1995	2122
55	1273	1656	1878	2031	2157
60	1313	1693	1913	2063	2186
65	1349	1725	1943	2090	2210
70	1382	1755	1969	2113	2229
75	1412	1781	1992	2132	2244
80	1440	1806	2013	2149	2258
85	1465	1828	2032	2163	2270
90	1488	1848	2048	2176	2282
95	1510	1866	2063	2186	2293
100	1530	1883	2077	2196	2304
105	1549	1898	2089	2205	2314
110	1566	1912	2100	2214	2324
115	1583	1926	2111	2222	2334
120	1598	1938	2121	2231	2344
125	1613	1950	2130	2239	2354

In order to show the deviations of the two gases from the ordinary perfect gas laws for mixtures, the values of f/NP have been calculated and are shown in Fig. 4.

It is difficult to give an estimate of the accuracy of the calculated fugacities. The errors introduced in the course of the calculations are certainly much less than the probable experimental error. Making reasonable but very liberal assumptions as to the experimental uncertainty, based on the irregularities in the curves of Δ (Equation 8) against N , we estimate the limit of error in the fugacities to be as follows.

1. The greatest errors occur in the values for argon at zero concentration, that is, for argon in pure ethylene. They range from a few hundredths of a per cent. at one atmosphere to a maximum of 7% at 125 atmospheres. With increasing mole fractions of argon the uncertainty in the fugacities at each pressure diminishes until in pure argon the error limit varies from a few hundredths of one per cent. at one atmosphere to 1.5% at 125 atmospheres.

2. For ethylene at zero concentration the error ranges from a few

hundredths of a per cent. at one atmosphere to 4.6% at 125 atmospheres, diminishing slightly with increasing mole fraction at each pressure. In pure ethylene the error ranges from zero to 3.5%.

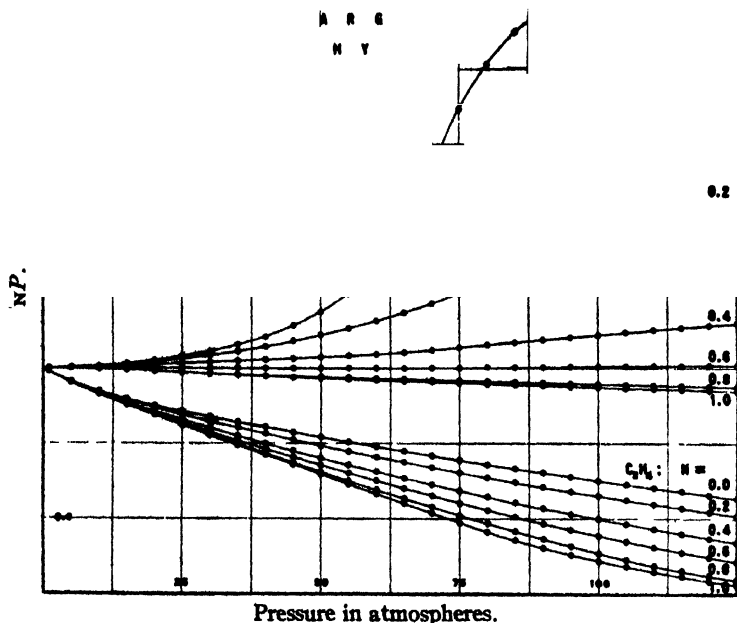


Fig. 4.—Graphical representation of the fugacities and deviations from the perfect gas law $f = NP$ of ethylene and argon in their mixtures.

Summary

In order to test the rule of Lewis and Randall, that the fugacity of a constituent in a mixture of gases is the product of the mole fraction and the fugacity of the pure constituent at the pressure of the mixture, the fugacities of ethylene and argon were calculated from the experimental data of Masson and Dolley. The rule was found to hold fairly well at low pressures. At about 50 atmospheres, however, the error of the fugacity calculated by the rule ranges from zero to 20%, depending on the mole fraction. At 100 atmospheres the errors range from zero to about 100%.

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THE HYDRATION OF SODIUM MONOMETAPHOSPHATE IN ALKALINE SOLUTION AT 75°. PHOSPHATE V

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Introduction

For almost a century it has been known through the work of Graham¹ that the phosphates, ortho-, pyro- and meta-, can be transformed from one to the other. His work at the time was an epoch-making contribution to the chemistry of phosphates, where even today it occupies a remarkably authoritative position.

During the intervening period attention has been directed more especially to the study of the orthophosphate and orthophosphoric acid, with a result of numerous, extensive and valuable researches. The chemistry of the meta- and pyrophosphates has not been as widely nor as satisfactorily developed. The nature of their inter-transformations and the conditions which influence them have been studied more particularly from the standpoint of the rate of hydration and the formulation of it.² To a limited extent the effects of concentration of acid and temperature upon the rate of hydration have been quantitatively investigated.³

No work, moreover, of a definite character has been done on the hydration of the metaphosphate in an alkaline solution. The lack of methods for determining the meta- and pyrophosphates has doubtless retarded the work in this range. The difficulty of obtaining containers which were unaffected by the alkaline solution has possibly contributed to the delay.

In the work which follows, a study of the alkaline hydration of sodium monometaphosphate to sodium pyrophosphate and sodium orthophosphate was undertaken. Pure silver flasks were used as containers. A method of separating and determining pyrophosphate in the presence of ortho- and metaphosphates was employed in following the progress of the hydration of metaphosphate to pyrophosphate. A method of separating

¹ Graham, *Phil. Trans.*, **123**, 253 (1833).

² (a) Sabatier, *Compt. rend.*, **106**, 63 (1888); (b) **108**, 734, 804 (1889); (c) Berthelot and André, *Compt. rend.*, **124**, 265 (1897); (d) **124**, 261 (1897); (e) Montemartini and Egidi, *Gazz. chim. ital.*, **31**, 394 (1903); (f) Balareff, *Z. anorg. Chem.*, **67**, 234 (1909); (g) **68**, 288 (1911); (h) **96**, 103 (1916); (i) **118**, 123 (1921); (j) Giran, *Ann. chim. phys.*, **30**, 203 (1903); (k) Holt and Meyers, *J. Chem. Soc.*, **99**, 385 (1911); (l) Aoyama, *J. Pharm. Soc. Japan*, **520**, 553 (1925); (m) Abbott, *THIS JOURNAL*, **31**, 763 (1909).

³ (a) Abbott, *THIS JOURNAL*, **31**, 763 (1909); (b) Beans and Kiehl, *THIS JOURNAL*, **49**, 1878 (1927); (c) Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926); (d) Kiehl and Hill, *THIS JOURNAL*, **49**, 123 (1927).

and determining orthophosphate was employed in following the progress of the hydration of metaphosphate to orthophosphate. The results of the investigation are given below.

Apparatus

Bath.—An oil-bath, sensitive to ± 0.01 at 75° , was used. The regulator was a twelve-foot, quarter-inch steel tube, entirely filled with mercury, coiled within the bath. This made and broke in the usual manner an electrical circuit by which the heating current was supplied.

Flasks.—The hydrations were studied in a silver vessel whose capacity was a little over a liter, constructed somewhat after the style of an Erlenmeyer flask. The stopper, made of silver, was ground to fit. Two silver tubes, for the removal of samples, extended through the stopper—similar in the arrangement to an ordinary wash bottle. These tubes were closed with silver plugs ground to fit. As a further precaution against evaporation, the stopper was sealed to the flask with a wax made of one part paraffin and one part carnauba wax. A piece of rubber tubing, closed at one end, was placed over each of the plugs and tubes.

Preparation of Materials

Sodium Monometaphosphate.—Sodium monometaphosphate was prepared by the method previously described.⁴ The dihydrate was obtained when the salt was further purified by thrice crystallizing it from distilled water. By drying it overnight at 100° in a Freas oven the anhydrous salt was prepared. Analyses were made for any remaining water, whereby the necessary corrections were made when and where they were required.

In order to determine if crystallization from water and subsequent heating at 100° would change the character of the salt heretofore described, qualitative tests were made and freezing-point depressions measured. Neither procedure indicated that the salt possessed properties different from those of the salt crystallized from fusion.

The water of hydration was determined by selecting a few large, quickly-dried crystals and finding the loss of weight by ignition. The following results were obtained.

TABLE I
ANALYSIS FOR WATER OF HYDRATION

Samples	No. 1	No. 2
Grams of crystals.....	1.8858	1.9217
Grams of anhydrous salt.....	1.3940	1.4189
Grams volatilized.....	0.4918	0.5028
Percentage of water of hydration.....	26.08	26.17
Percentage of water of hydration (theoretical)....	26.10	

Calculations gave results which corresponded to the formula $\text{NaPO}_3 \cdot 2\text{H}_2\text{O}$.

The following crystallographic measurements were made by Professor Paul Kerr of the Geology Department in Columbia University. "The crystals are triclinic with the following angular measurements between faces:

⁴ Beans and Kiehl, *THIS JOURNAL*, 49, 1878 (1927).

TABLE II
CRYSTALLOGRAPHIC MEASUREMENTS

Faces		Angles measured	
001	100	64°	16'
100	010	73°	28'
010	110	42°	53'
100	110	62°	55'
001	010	82°	33'

"There is a perfect cleavage parallel to (001). On removal from the solution for measurement the crystals soon acquire a white powdery coating which darkens the reflection signals on the goniometer considerably and reduces the accuracy of measurement.

"The mean index of refraction is 1.400 and the double refraction is about 0.009. The material is biaxial with a large axial angle and one of the optic axes is nearly perpendicular to the cleavage (001). The acute bisectrix of the optic angle corresponds to γ , the slow ray, in dispersion $p > v$."

Sodium Pyrophosphate, $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$.—Normal sodium pyrophosphate was crystallized three times from distilled water and carefully dried.

Disodium Orthophosphate.—Disodium orthophosphate was prepared and the product standardized by the method described by Hansen and one of us.⁵

Sodium Hydroxide.—Solutions of sodium hydroxide used for hydration were made from a saturated solution of the purest available sodium hydroxide. This solution was filtered through a dry filter paper and diluted to a convenient concentration. It was then standardized by Bureau of Standards benzoic acid.

Zinc Acetate Reagent.—Zinc acetate of pure quality, free from phosphate, was used. Eighty grams of the zinc acetate was dissolved in distilled water and diluted to two liters. Two hundred and fifty cubic centimeters of glacial acetic acid were then added. This gave about a 0.2 *M* zinc acetate solution with a hydrogen-ion concentration of 5×10^{-4} moles per liter.

Method of Procedure

Separation of Pyrophosphate from Orthophosphate and the Determination of Pyrophosphate.—In order to determine the extent of hydration in alkaline solution, it was necessary to separate the pyrophosphate formed. After trying many other precipitants, the zinc acetate reagent was found to be the most satisfactory. Orthophosphate gives no precipitate under the conditions described below, except for concentrations greater than 0.1 mole per liter. It, therefore, was successfully used in the separation, even though it did not give a crystalline precipitate, provided the concentration of hydrogen ion was carefully controlled.

Thirty to forty cubic centimeters of zinc acetate reagent was added to the solution containing the pyrophosphate, whose hydrogen-ion concentration was adjusted to 5×10^{-4} moles per liter by the addition of acetic acid and water, thereby making a total of 120 cc. After standing

⁵ Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926).

for three minutes it was centrifuged for three minutes. The clear liquid was then decanted through a weighed Gooch crucible. Fifty cubic centimeters of distilled water was added with stirring to the precipitate, which was again centrifuged and transferred to the Gooch crucible. Enough 2 *M* sodium hydroxide was added thereafter to dissolve the precipitate on the filter. After dilution to 75 cc. by washings from the filter and Gooch crucible, an equal volume of a solution, so prepared that it contained 4 *M* acetic acid and 0.5 *M* zinc acetate, was added to reprecipitate the pyrophosphate. This solution was centrifuged again and decanted through a weighed Gooch crucible. After decanting the clear solution and one washing with water, the precipitate was transferred to the Gooch crucible with repeated washing, filtered, dried and ignited with a Méker burner for half an hour.

Composition of Ignited Precipitate.—In order to determine whether the precipitated zinc pyrophosphate would give after ignition a product invariable in composition, several quantities of it were prepared and samples from each ignited lot were analyzed. The results of the zinc and phosphorus determinations from two such samples are given below.

Table III shows the amount of zinc found in the ignited precipitate by the potassium ferrocyanide method.

TABLE III
ZINC IN THE PYROPHOSPHATE PRECIPITATE

Sample	G. ppt. taken	G. Zn found
1	0.3026	0.1293
2	.2991	.1278

The phosphorus was determined by the standard gravimetric procedure after complete hydration by boiling with nitric acid. The following values were obtained.

TABLE IV
PHOSPHORUS IN PYROPHOSPHATE PRECIPITATE

Sample	G. ppt. taken	G. $Mg_3P_2O_7$	Equiv. to g. P
1	0.3853	0.2815	0.0784
2	.3286	.2408	.0670

The ratio of atoms of zinc to atoms of phosphorus in the first case is 1 to 0.997, in the second 1 to 0.993. From the percentage of both zinc and phosphorus in the ignited precipitate and from the ratio above, the empirical formula of the ignited zinc precipitate corresponds to $Zn_2P_2O_7$.

In order to determine if the acetic acid used would be sufficient to accelerate the hydration of metaphosphate at room temperature to interfere in the pyrophosphate determination, strong solutions of acetic acid were added to 0.2 *M* sodium monometaphosphate, which was allowed to stand for several days at room temperature. No precipitate with the zinc acetate reagent resulted. Mixtures of sodium acetate, acetic acid, zinc acetate

0.2 *M* metaphosphate and 0.08 *M* orthophosphate, set aside at room temperature for several days, likewise gave no precipitate under the conditions of separation and determination of pyrophosphate.

Determination of Pyrophosphate.—To test the method the following were a few of the determinations which were made on aqueous solutions of sodium pyrophosphate of known value.

TABLE V
PYROPHOSPHATE BY ZINC ACETATE REAGENT

Mg. P taken as pyro-	31.04	31.04	31.04	31.04	31.04
Mg. P found as pyro-	31.05	31.09	31.05	31.08	30.82 30.74
Mg. P taken as pyro-	62.08	62.08	62.08	62.08	62.08 62.08
Mg. P found as pyro-	62.27	61.88	62.10	62.55	61.89 61.85
Mg. P taken as pyro-	153.0	153.0	153.0	153.0	
Mg. P found as pyro-	152.9	153.1	152.8	152.9	

The average deviation in parts per thousand by the above method for the analysis on 31.04 mg. of phosphorus as pyrophosphate is 2; for 62.08 mg. of phosphorus it is 3.

Determination of Orthophosphate in Filtrate.—In the actual hydration after separating pyrophosphate the filtrate contained zinc ion and metaphosphate ion which might offer the possibility of trouble. For assurance it was necessary, therefore, that this filtrate without orthophosphate present give no precipitate under conditions for determining orthophosphate, that metaphosphate be not hydrated in the alkaline solution during the process, and that no precipitate be formed with meta- and orthophosphates present and the magnesia mixture alone absent. Accordingly, no precipitate had formed after standing six days when a portion of plain filtrate without ortho- or metaphosphate present was made alkaline with NH_4OH and treated with the appropriate quantity of magnesia mixture. Likewise, when metaphosphate was added to the plain filtrate and treated as above no precipitate had occurred in fifteen days. Furthermore, with orthophosphate present without the magnesia mixture only, no precipitate had formed during four days.

In the following paragraph the method is outlined for determining orthophosphate in the filtrate from analysis of pyrophosphate in the course of the hydrations.

Sufficient 15 *M* ammonium hydroxide was added to the pyrophosphate filtrate to re-dissolve the zinc precipitate at first formed. Twenty cubic centimeters of 5 *M* ammonium chloride was added. After standing for three hours it was filtered, dissolved and re-precipitated by the standard method in a total volume of 125 cc. After it stood at least three hours it was filtered, ignited and weighed as usual.

Table VI shows some of the determinations of orthophosphate made upon the pyrophosphate filtrate with and without metaphosphate present.

TABLE VI
ORTHOPHOSPHATE IN PYROPHOSPHATE FILTRATE

Mg. P taken as meta-	Mg. P taken as ortho-	Mg. P found as ortho-
388	31.49	33.19
388	31.49	32.45
155	31.49	31.60
155	59.92	60.97
139	14.98	15.42
77	38.80	39.00
77	38.80	38.90
None	31.49	31.48
None	31.49	31.49

Table VII contains a few of the determinations made directly upon orthophosphate solutions with meta- as indicated.

TABLE VII
ORTHOPHOSPHATE DIRECTLY

Mg. P taken as meta-	Mg. P taken as ortho-	Mg. P found as ortho-
217	14.98	15.42
217	59.92	61.03
139	59.92	60.89
77	38.80	38.95
None	59.92	59.47

The values in Tables VI and VII are representative of the many results obtained in testing the method, over the complete range of metaphosphate concentration in the filtrate from the pyrophosphate determination. The average deviation from the amount added is 25 parts per thousand. When tests were made in orthophosphate solutions directly the average deviation was of the order of that from the filtrate of the pyrophosphate with the same amount of metaphosphate present. Inasmuch as the amount of metaphosphate present at any one time did not exceed 140 mg., the average deviation was found from a number of determinations to be 15 parts per thousand.

Test of the Method under Conditions of Hydration.—Whether zinc acetate reagent would precipitate pyrophosphate quantitatively in the concentrations and under the conditions of the hydrations is yet to be demonstrated. Solutions of meta-, pyro- and orthophosphates and sodium hydroxide in concentrations to be found in the hydrations were made at 20° and taken from a buret. These were analyzed for pyro- and orthophosphates. Where 2 *M* sodium hydroxide was used enough glacial acetic acid was added to give a concentration of hydrogen ion of 5×10^{-4} moles per liter.

Table VIII which follows gives the milligrams of phosphorus taken as meta-, pyro- and orthophosphates and the milligrams of phosphorus found as pyro- and orthophosphates.

TABLE VIII
DETERMINATION OF PYRO- AND ORTHOPHOSPHATES

	Molar NaOH	P taken as meta-	P taken as pyro-	P found as pyro-	P taken as ortho-	P found as ortho-
1	2.0	217	15.42	14.90	14.98	15.02
2	2.0	139	15.42	14.93	None	None
3	1.0	124	6.21	6.16	None	None
4	1.5	124	108.64	108.78	93.12	92.82
5	2.0	108	46.30	46.17	14.98	15.06
6	2.0	108	30.85	30.85	None	None
7	0.5	93	45.56	47.05	31.04	31.24
8	2.0	46	61.70	61.27	99.86	101.01
9	2.0	45	61.70	61.66	44.94	46.40
10	2.0	31	77.12	78.28	44.94	46.40
11	2.0	15	77.12	77.34	59.92	60.97
12	2.0	15	77.12	76.85	5.99	5.90
13	None	None	77.60	77.70	31.04	None
14	None	None	77.60	77.24	31.04	None
15	None	None	77.60	76.97	None	None
16	None	None	31.04	30.92	77.60	78.64
17	None	None	31.04	30.41	31.04	31.02
18	None	None	31.04	31.06	62.08	62.13
19	None	None	77.60	77.30	77.60	76.39
20	None	None	None	None	31.04	31.49
21	None	None	None	None	31.04	31.21
22	None	None	None	None	59.92	59.47
23	2.0	None	92.60	92.55	59.92	60.00
24	None	None	63.00	63.18	None	None
25	None	None	315.00	318.50	None	None
26	None	None	315.00	318.80	None	None
27	None	None	31.00	31.21	None	None

In the above table the average deviation from amount added is 9 parts per 1000 for pyrophosphate and 11 parts per 1000 for orthophosphate.

Experimental Part

The temperature selected for conducting the hydrations was 75°. Solutions were made in a two-liter, calibrated flask with as little contact with air as possible. A sample of each solution was then taken for analysis and for a pycnometric density determination. The remainder was placed in two silver flasks and hydrated in duplicate. The density of each solu-

TABLE IX
SOLUTIONS STUDIED

Soln.	Concn. NaPO ₃ moles per l.	Concn. NaOH moles per l.	Sp. gr. 15.5°/15.5° at beginning	Sp. gr. 15.5°/15.5° at end
A ₁	0.100	0.500	1.031	1.032
B ₁	.200	.500	1.039	1.040
D ₁	.100	2.000	1.093	1.093
E ₁	.200	2.000	1.101	1.101

tion was again determined at the end of each experiment and no change in any case greater than one part in one thousand was observed.

In the beginning from time to time small samples were taken through the silver tubes and tested for pyrophosphate and orthophosphate. When they were found a sample was drawn into a small flask which was quickly stoppered and cooled to 20°. By means of a calibrated pipet 25 cc. was taken and analyzed as described above. The following tables give the percentages of pyrophosphate and orthophosphate found in the solutions at the stated intervals.

In the heading for each table the weight of $\text{Zn}_2\text{P}_2\text{O}_7$ equivalent to the total phosphorus in 25 cc. of solution is given. This we shall call *M*. Similarly the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ will be designated *N*. The calculation of the percentage of phosphorus transformed to pyrophosphate and orthophosphate, respectively, becomes simple when the amounts of $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{Mg}_2\text{P}_2\text{O}_7$ are actually known for each 25cc. portion.

TABLE X
SOLUTION A

$\text{NaPO}_3 = 0.099 \text{ M}$; $\text{NaOH} = 0.500 \text{ M}$; $\text{M} = 0.3777 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\text{N} = 0.2759 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% meta- by diff.
1	18.5	0.0189	5.0
2	23.5	.0267	7.1
3	29.5	.0443	11.6	0.0151	5.5	82.9
4	41.5	.0603	15.9	.0223	8.1	76.0
5	65.5	.0872	23.0	.0339	12.3	64.7
6	89.5	.1151	30.5	.0460	16.7	52.8
7	113.5	.1384	36.6	.0561	20.4	43.0
8	137.5	.1549	41.0
9	185.5	.1880	49.8	.0756	27.4	22.8
10	275.5	.2231	59.1	.0864	31.3	9.6
11	353.50926	33.6	..
12	449.5	.2357	62.4	.0958	34.7	2.9
13	545.5	.2375	62.9	.0958	34.7	2.4
14	713.5	.2416	64.0	.0946	34.3	1.7
15	881.5	.2454	65.0	.0933	33.9	1.8
16	915.5	.2456	65.0
17	1002.5	.2409	63.8	.0949	34.4	1.8
18	1123.0	.2430	64.4	.0957	34.7	0.9

Discussion of Results

In the alkaline hydration of sodium monometaphosphate, and under the conditions of our experiments, both orthophosphate and pyrophosphate are formed. This was shown by the analyses of the solutions. It was further shown by crystals that separated from the completely hydrated solutions. When these completely hydrated solutions were allowed to stand for several days at room temperature, sodium pyrophosphate

crystallized. The large crystals could be separated easily and washed free of mother liquor and analyzed. If, however, some of the completely

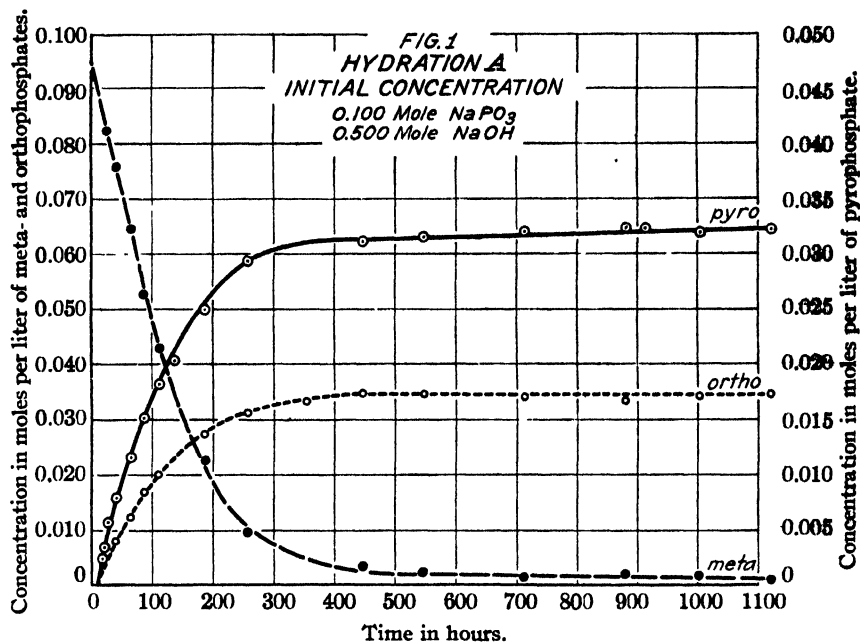


TABLE XI
SOLUTION A₂^a

$\text{NaPO}_3 = 0.099 \text{ M}$; $\text{NaOH} = 0.500 \text{ M}$; $\text{M} = 0.3777 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\text{N} = 0.2759 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% meta-by diff.
1	18.5	0.0190	3.1
2	23.5	.0267	7.1
3	29.5	.0446	11.8	0.0151	5.5	82.7
4	41.5	.0610	16.1	.0217	7.9	76.0
5	65.5	.0865	22.0	.0334	12.1	65.0
6	89.5	.1146	30.3	.0473	17.1	52.6
7	113.5	.1380	36.5	.0555	20.1	43.4
8	137.5	.1540	40.8
9	185.5	.1880	49.8	.0750	27.2	23.0
10	257.5	.2220	58.8	.0864	31.3	9.9
11	353.50926	33.2	..
12	449.5	.2338	61.9	.0960	34.8	3.3
13	545.5	.2398	63.4	.0955	34.5	2.1
14	713.5	.2460	65.1	.0936	33.0	2.0
15	881.5	.2457	65.1	.0940	34.1	0.8

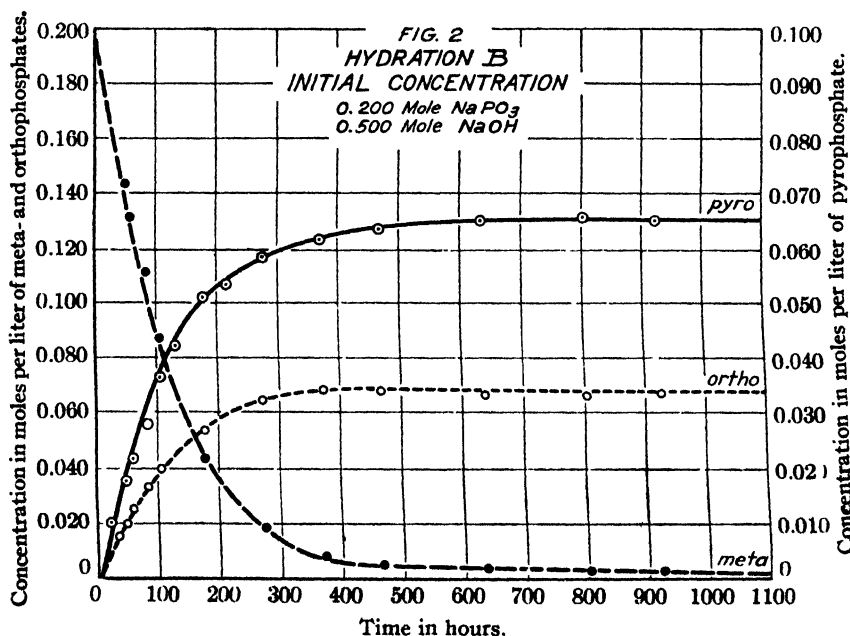
^a Solution A₂ is a duplicate of A given to show the reproducibility of results and the dependability of the method.

TABLE XII

SOLUTION B

$\text{NaPO}_3 = 0.200 \text{ M}$; $\text{NaOH} = 0.500 \text{ M}$; $\text{M} = 0.7620 \text{ g. Zn}_3\text{P}_2\text{O}_7$; $\text{N} = 0.5566 \text{ g. Mg}_3\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_3\text{P}_2\text{O}_7 \text{ g.}$	% hydrated to pyro-	$\text{Mg}_3\text{P}_2\text{O}_7 \text{ g.}$	% hydrated to ortho-	% of meta-by diff.
1	24	0.0782	10.3
2	36	0.0416	7.5	72.5
3	48	.1334	17.5	.0559	10.0	72.5
4	60	.1655	21.7	.0700	12.5	65.8
5	84	.2116	27.8	.0933	16.7	55.5
6	108	.2773	36.4	.1113	20.0	43.6
7	131	.3203	42.1
8	180	.3883	51.0	.1507	27.1	21.9
9	216	.4091	53.7
10	276	.4457	58.5	.1793	32.2	9.3
11	372	.4713	61.9	.1899	34.0	4.1
12	468	.4858	63.7	.1886	33.9	2.4
13	636	.4975	65.2	.1836	33.0	1.8
14	804	.5020	65.8	.1834	33.0	1.2
15	925	.4947	65.0	.1871	33.6	1.4
16	1298	.5014	65.7	.1881	33.8	0.5



hydrated solution was allowed to evaporate at room temperature, at first sodium pyrophosphate only crystallized. When the solution became more concentrated orthophosphate crystallized also. When both types of crystals were carefully freed from the mother liquor and dried, the

sodium orthophosphate crystals became visibly efflorescent within a few hours, while the pyrophosphate crystals remained unchanged. These

TABLE XIII

SOLUTION D

$\text{NaPO}_3 = 0.100\text{ }M$; $\text{NaOH} = 2.00\text{ }M$; $M = 0.3810\text{ g. Zn}_2\text{P}_2\text{O}_7$; $N = 0.2783\text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% of meta-by diff.
1	23	0.0421	11.1
2	31	.0735	19.3	0.0278	10.0	70.7
3	45	.1030	27.0	.0556	20.0	53.0
4	59	.1372	36.0	.0665	23.9	40.1
5	71	.1715	45.0	.0750	26.9	28.1
6	92	.1932	50.7	.0852	30.6	18.7
7	116	.2129	55.8	.0929	33.3	10.9
8	151	.2249	59.0	.0952	34.1	6.9
9	188	.2400	63.0	.0958	34.4	2.6
10	260	.2478	65.0	.0955	34.4	0.6
11	380	.2494	65.4	.0957	34.4	.2

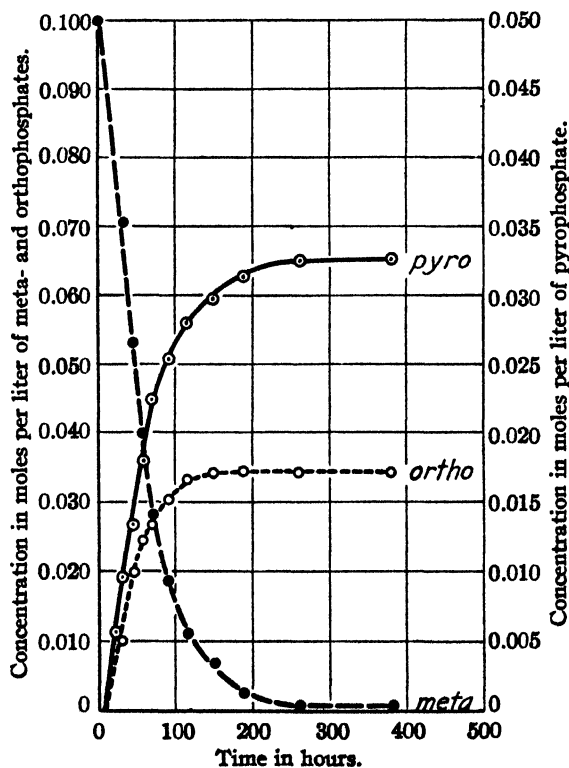


Fig. 3.—Hydration D. Initial concentration. $0.100\text{ }M$ NaPO_3 , $2.00\text{ }M$ NaOH .

TABLE XIV

SOLUTION E

 NaPO_3 0.200 M; NaOH = 2.00 M; M = 0.7631 g. $\text{Zn}_3\text{P}_2\text{O}_7$; N = 0.5584 g.
 $\text{Mg}_3\text{P}_2\text{O}_7$

	Hours	$\text{Zn}_3\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_3\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% of meta- by diff.
1	6.0	0.0373	4.9	0.0126	2.2	92.9
2	15.5	.1013	13.3	.0688	12.3	74.4
3	32.5	.1657	21.7	.0867	15.7	62.6
4	45.5	.2280	29.8	.1218	21.8	48.4
5	57.51451	26.1	..
6	76.5	.3557	46.6	.1639	29.4	24.0
7	94.5	.4015	52.7	.1788	32.0	15.3
8	118.5	.4455	58.5	.1908	34.2	7.3
9	168.5	.4973	65.3	.1881	33.2	1.0
10	292.5	.5011	65.7	.1893	33.8	0.5

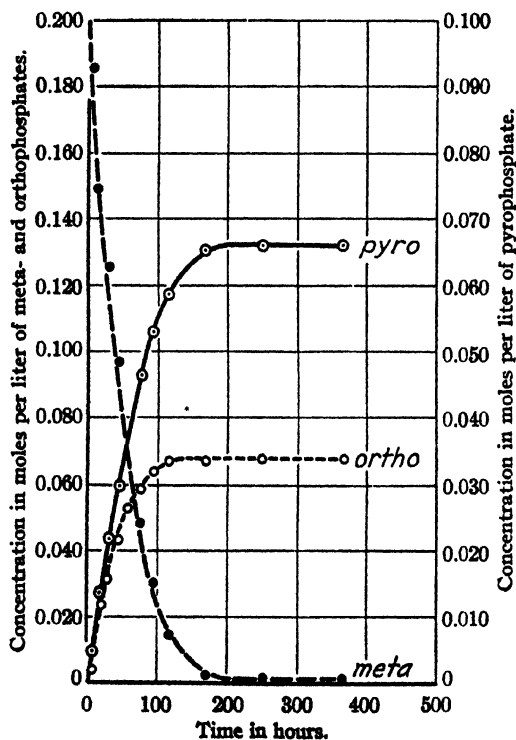


Fig. 4.—Hydration E. Initial concentration. 0.200 M NaPO_3 , 2.00 M NaOH .

efflorescent crystals were separated from the others and tested. They were orthophosphate crystals.

Since orthophosphate and pyrophosphate were both found when the

metaphosphate was completely hydrated, and since they appeared in each hydration to reach a final value of approximately 34% of the phosphorus in the form of orthophosphate, it would seem that the pyrophosphate and orthophosphate were either end-products or in equilibrium with each other.

That orthophosphate and pyrophosphate were not in equilibrium was shown by the following experiments:

A duplicate of Hydration B was kept in the 75° bath for 419 hours after the metaphosphate had disappeared. No change in the ratio of pyrophosphate to orthophosphate was found. The solution was then placed in the 100° bath and analyzed from time to time for 414 hours more. There was no change in the ratio of pyrophosphate to orthophosphate.

In the D and E hydrations four times as much sodium hydroxide was used as in the A and B hydrations, but the final ratio of pyrophosphate to orthophosphate was the same.

A solution called C, containing 0.5 *M* sodium hydroxide and 0.1 *M* disodium orthophosphate, was kept in the 75° bath for seven days without producing any pyrophosphate.

Another solution, called F, was made of 2.0 *M* sodium hydroxide, and 0.1 *M* phosphorus as ortho- and pyrophosphates. Twenty-five per cent. of the phosphorus was in the form of normal sodium pyrophosphate and 75% disodium orthophosphate. It remained in the 75° bath for 23 days without any orthophosphate reacting to form pyrophosphate, or pyrophosphate to form orthophosphate.

Another solution, called G, was made of 0.2 *M* phosphorus in the form of ortho- and metaphosphates with 2.0 *M* sodium hydroxide. One-third was sodium monometaphosphate and two-thirds disodium orthophosphate. This was kept in the boiling bath for 22 days. The pyrophosphate obtained was that which would result from the hydration of the monometaphosphate added as shown in the preceding tables while the orthophosphate was increased by 34% of the amount of phosphorus added as monometaphosphate. No orthophosphate was transformed to pyrophosphate.

In order to determine if pyrophosphate would hydrate to orthophosphate a solution of 0.2 *M* sodium pyrophosphate and 2.0 *M* sodium hydroxide was kept in the boiling bath for 22 days without a trace of orthophosphate being formed.

A 0.2 *M* sodium pyrophosphate in a 4.0 *M* sodium hydroxide solution was kept in the boiling bath for four days. No orthophosphate was produced.

Since neither increase of temperature nor change of concentration of phosphates and sodium hydroxide altered the ratio of pyrophosphate to

orthophosphate, and since pyrophosphate was not formed from orthophosphate in solution, and since orthophosphate was not formed from pyrophosphate, it seemed reasonably certain that no equilibrium existed under the conditions of our experiments.

All of these experiments were carried out in pure silver flasks.

Graham⁶ states: "But pyrophosphate of soda may be boiled with caustic soda for hours without sensible alteration, provided the solution is not evaporated to dryness; and it crystallizes afterwards in its original form, exhibiting no disposition whatever to form sub-pyrophosphate."

Therefore, since the orthophosphate did not appear from the hydration of pyrophosphate, it must have been produced by the hydration of metaphosphate, and since the pyrophosphate which was present in the hydrations did not result from the dehydration of orthophosphate, it must have occurred from the hydration of the metaphosphate.

It is of interest to note that the orthophosphate and the pyrophosphate were produced in equimolecular quantities. From our work it seems that for every three moles of the sodium monometaphosphate hydrated one mole of orthophosphate and one mole of pyrophosphate were produced simultaneously.



This may mean two independent reactions or one single involved reaction; but since the experimentation has not covered a wide enough range of temperature the decision cannot be made. However, one may conceive of the possibility of two different rates of hydration, if there are two reactions, each affected to a different degree by temperature. Work is planned to elucidate the mechanism and clear this point.

The foregoing experimental data and Figures 1, 2, 3 and 4 demonstrate that an increase in the hydroxyl-ion concentration increases the rate of hydration.

Summary

1. Sodium monometaphosphate dihydrate was prepared.
2. A method of determining pyrophosphate in the presence of meta- and orthophosphate was developed.
3. Sodium monometaphosphate was hydrated to sodium pyrophosphate and sodium orthophosphate in alkaline solution at 75° in silver flasks.
4. Sodium pyrophosphate is an end-product and sodium orthophosphate is an end-product, in the alkaline hydration of sodium monometaphosphate when reactions are carried out in silver flasks.
5. The increase of the sodium hydroxide concentration increased the rate of hydration.

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⁶ Ref. 1, p. 255.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ACTION OF LIGHT ON CHLORINE

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I. Introduction

A comparison of the photochemical literature on the reactions and other properties of illuminated chlorine on one side and of the results of a more physical investigation of its absorption spectrum on the other, indicates that, at present, a certain controversy exists between two main opinions on the nature of the primary action of light on chlorine.

Several studies of the absorption spectra of the halogens, of the more recent ones particularly that of Kuhn,² demonstrated the existence of series of absorption bands converging on the short-wave side to a limit, from which a continuous absorption extends toward the ultraviolet. On the basis of these observations Franck³ suggested that chlorine and other halogen molecules are dissociated into atoms—a normal and an excited atom—on absorption of radiation frequencies belonging to the continuous absorption region and that absorption in the region of the band spectrum causes formation of activated molecules, capable in general of reëmission of absorbed light energy as fluorescence radiation. Franck's conclusions were later confirmed by Dymond⁴ who showed that fluorescence is emitted by iodine molecules only on absorption of light of longer wave length than 5000 Å.—the convergence limit of this halogen. It may be pointed out that, according to physical researches, a further condition for the realization of fluorescence in halogen vapors is their low pressure. Thus, Wood and Speace⁵ found that excited iodine molecules can be deactivated on collisions not only in presence of foreign gases but also in pure iodine vapor.

A number of different theories on the nature of the primary action of light on chlorine have been advanced recently by several photochemists, their common experimental basis being the observation of Coehn and Jung⁶ that a pure and dry mixture of chlorine and hydrogen does not react on illumination by visible and near ultraviolet light. The theory of Norrish,⁷ however, who located the chemical action of light on chlorine in the water-chlorine film on the walls of the containing vessel, has been recently disproved by decisive experiments of Coehn and Heymer.⁸ Fur-

¹ International Research Fellow.

² Kuhn, *Z. Physik*, **39**, 77 (1926).

³ Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

⁴ Dymond, *Z. Physik*, **34**, 553 (1925).

⁵ Wood and Speace, *Physik. Z.*, **15**, 317 (1914).

⁶ Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

⁷ Norrish, *J. Chem. Soc.*, **127**, 2317 (1925).

⁸ Coehn and Heymer, *Ber.*, **59B**, 1794 (1926).

ther, primary formation of activated chlorine molecules⁹ or of chlorine atoms⁶ has been occasionally suggested, the catalytic action of water being attributed to secondary processes. These theories coincide, at least in broad terms, with the deductions from the study of the absorption spectrum of chlorine, since, as Franck³ pointed out, dissociation into atoms must be preceded by activation of chlorine molecules. Only further investigations can decide to which of these stages the photochemical reactivity of chlorine should be attributed. A distinctly different theory has been advanced by Weigert,^{10,11} who suggested that water molecules are necessary for the accomplishment of the *primary* photochemical process in chlorine. If this latter is absolutely pure, all absorbed light energy is reëmitted by chlorine molecules as isochromatic fluorescence and only in presence of water or certain other molecules can the absorbed radiation be converted into chemical energy or into heat. The special nature of this action of foreign molecules was also discussed by Weigert and he suggested for instance that, in the hydrogen-chlorine reaction, water acts through its di-pole nature, facilitating an inner photo-electric effect between hydrogen and chlorine. As an important support of his theory Weigert cited the results of investigations on the Budde effect—the expansion of chlorine gas on illumination. Since Budde's¹² discovery, more recent investigations have demonstrated that the effect is due entirely to the conversion of absorbed light energy in chlorine into heat.^{13,14} Further, it was found that *dry* chlorine shows a very small Budde effect and that the effect can be increased considerably by admission of some moisture to the gas.¹⁵ Ludlam¹⁶ arrived at a similar conclusion, experimenting with bromine.

In the opinion of Weigert this observed absence of the heating of dry chlorine is a direct evidence that the absorbed light energy can be converted into heat only in presence of moisture and is reëmitted as fluorescence by pure gas. Lewis and Rideal¹⁷ went even further. On investigating the Budde effect in bromine vapor, they suggested that only a definite molecular compound $\text{Br}_2\text{-H}_2\text{O}$ is photosensitive and that all light absorbed by simple bromine molecules is re-radiated again as fluorescence.

Summarizing, it may be pointed out that all theories which assume the presence of foreign molecules to be necessary for the primary photo-

⁹ Chapman, *Trans. Faraday Soc.*, 21, 547 (1925).

¹⁰ Weigert, *Z. physik. Chem.*, 106, 426 (1923).

¹¹ Compare also Cathala, *Compt. rend.*, 181, 33 (1925).

¹² Budde, *J. prakt. Chem.*, 7, 376 (1873).

¹³ Richardson, *Phil. Mag.*, [5] 32, 221 (1891).

¹⁴ Bevan, *Trans. Roy. Soc. (London)*, 202, 90 (1904).

¹⁵ Shenstone, *J. Chem. Soc.*, 71, 471 (1897).

¹⁶ Ludlam, *Proc. Roy. Soc. Edinburgh*, 34, 197 (1924).

¹⁷ Lewis and Rideal, *J. Chem. Soc.*, 128, 583 (1926).

chemical process assume at the same time that pure chlorine (and similarly bromine) does fluoresce. With the test of this latter conclusion we are concerned in the experiments now to be described.

II. Experimental Arrangement

In order to obtain gas of a known photochemical inactivity the method of Coehn and Jung⁶ of purification and drying of chlorine was closely followed. The apparatus consisted of a distilling arrangement for chlorine, of a quartz spiral manometer (quartz-Pyrex graded seal being used) and of two cylindrical vessels 23×3.5 cm. with sealed-on, optically clear Pyrex glass plates. These latter were necessary since, in search of chlorine fluorescence, all light from the illuminating source scattered on glass surfaces should be avoided as far as possible. The process of sealing-on proved to be not very difficult and although the edges of the plates were slightly damaged, their middle areas of about 2 cm. diameter remained entirely intact. Each vessel had two side tubes, one of which contained an inner glass seal separating a small volume (about 0.75 cc.) filled with water vapor at atmospheric pressure, the other being used for freezing out chlorine in some of the experiments. Stopcocks in the part of the apparatus behind the high-vacuum pump were entirely avoided; instead, inner glass seals operated by iron cores (enclosed in glass) and constriction for sealing-off were used. The whole apparatus, including the manometer, was baked out in a vacuum¹⁸ on two successive days, the test for tightness being that the pressure in the McLeod gauge did not increase overnight to more than 10^{-6} mm. The mercury-vapor trap was cooled by liquid air only during the second baking out and subsequent operations.

Chlorine from a half-empty chlorine tank was three times distilled in a vacuum at -112° (the temperature of melting carbon disulfide). Each time only about three-fourths of the chlorine was distilled over, the rest being sealed off. Finally, chlorine was condensed in the side tubes of the cylindrical vessels and these were sealed off from the rest of the apparatus. Of three attempted fillings only two could be carried out successfully. The first time chlorine of about 500 mm. pressure was prepared and preliminary measurements were taken. These results, although less exact, confirm entirely the final experiments with the third filling and chlorine of about 2 atmospheres' pressure.

III. Absorption of Light in Moist and Dry Chlorine

It may be concluded from Kuhn's² description of his experimental arrangement that he worked with fairly dry chlorine. It appeared to be of interest, nevertheless, to measure the wave length of the bands' convergence limit in the available chlorine of highest purity. For photographs of the chlorine absorption spectrum a Hilger glass spectograph, with a large direct vision prism inserted to increase the dispersion, was employed.¹⁹ Since the chlorine layer used was only 23 cm. long, the light absorption in the green was very weak even at 2 atmospheres' pressure. Therefore, the measurement of single bands with subsequent calculation of the convergence limit had to be abandoned. Still, study of the plates with a micrometer, as also curves made on the densitometer, permitted

¹⁸ For details compare Dushman, *High Vacuum Technique*, *Gen. Elec. Rev.*, Schenectady, 1922.

¹⁹ The author is indebted to Professor A. Shenstone of the Department of Physics for his kind advice and help during this part of the work.

an approximate determination of the convergence limit at 4790 Å. The reference spectrum used was that of an iron arc. The accuracy of this determination is about 10 Å. (1 mm. on the plates), so that the result obtained is to be considered identical with Kuhn's more exact value 4785 Å. Determinations of absorption coefficients of chlorine in monochromatic light of different wave lengths were carried out with unusual precision by Halban and Siedentopf.²⁰ They studied also the influence of moisture and found in light of three different wave lengths no appreciable difference between moist and fairly dry chlorine. A question which is not decided by these experiments and which is of importance for the following discussion is whether the total absorption in polychromatic light is markedly different in very dry and in moist chlorine. For the following measurements the glass vessels containing chlorine were placed in a blackened box with two openings rigidly adjusted on an optical bench. As light source a 100-watt Pointolite lamp was used, which in order to increase the intensity of shorter wave lengths was overloaded and burned on 1400 m. amps. and 115 volts. A system of lenses and diaphragms isolated a parallel beam of light, the square section of which was about 2.5 sq. cm. Immediately behind the chlorine vessel was placed a Moll thermopile of surface (3.14 sq. cm.) larger than the area of the light beam. The only light filter used for these and later experiments was a concentrated solution of ferrous sulfate (and a small quantity of hydrazine sulfate) which absorbed infra-red and a part of the extreme red radiation. Table I gives the results of measurements with chlorine of two atmospheres' pressure.

TABLE I
LIGHT ABSORPTION IN CHLORINE; PER CENT. OF THE TOTAL RADIATION

Dry chlorine	8.45; 9.95; 8.22; 8.40; av. 8.75
Moist chlorine	9.89; 7.91; av. 8.90

Each of these values is an average of about 20 single readings, half of them with the vessel filled with chlorine, half with the empty vessel, chlorine being frozen out by liquid air. The deviations of the values given are rather large—10% and more from the final averages. They are due not to the inexactness of the thermopile readings, but to the impossibility of keeping the light intensity constant to more than 1-2% during the longer time intervals necessary for freezing out and warming up of chlorine and eventually of water, this being admitted to the chlorine by breaking the inner glass seals mentioned earlier.

IV. Fluorescence of Dry Chlorine

The optical arrangement described in the former section was used also for the study of chlorine fluorescence. This part of the work included

²⁰ Halban and Siedentopf, *Z. physik. Chem.*, 103, 71 (1923).

experiments with the thermopile and spectrophotographic tests. The determination of the light absorption in chlorine was carried out with the sensitivity of the thermopile-galvanometer system reduced to 7.15% by series and shunt resistances. In order to test this calculated ratio of sensitivities, the light intensity of a special standard lamp was measured with full and reduced sensitivity. The ratio of scale deflections so determined was practically identical with the calculated, 0.073. The thermopile with full sensitivity of the circuit was placed at a distance of 1 cm. from the side wall of the chlorine vessel at a right angle to the light beam. Assuming a uniform distribution of fluorescence over the hypothetical radiating surface (of which the thermopile is a part) (399 sq. cm.), 0.0082 of the total emitted radiation should fall on the light sensitive surface of the thermopile. This calculation is somewhat unfavorable, since the thermopile was put close to that end of the vessel where the light beam entered and a greater part of the fluorescence should be concentrated here on account of the greater light absorption in the initial layers of chlorine. Further, in front of the thermopile was a polished metallic cone of 1 cm. length and 4 sq. cm. open front surface. If all light falling on the side walls of the cone was reflected to the light-sensitive surface of the thermopile, then the above fraction should be increased to about 0.013. The scale deflection corresponding to the light energy absorbed by chlorine was on the average 16.1 mm. (with reduced sensitivity). Thus, if all the light absorbed is reëmitted by dry chlorine as fluorescence, a deflection of at least 1.85 mm. should be expected. Measurements with the vessel filled with chlorine and with the empty vessel yielded 0.43 and 0.31 mm., respectively, as averages of about 20 single readings for each value. The single readings fluctuated between -0.1 and $+0.7$ mm.

There were good grounds for believing that even these small deflections—their difference ("the fluorescence") does not amount to more than 5% of the calculated value—are due to some heating effects on illumination rather than to emission of visible light, since, on visual observation, the chlorine vessel remained entirely dark when the light beam was passed through it.

The Hilger spectrograph, without the additional prism and with the slit wide open, was adjusted in the box at right angles to the light beam and at 2 cm. distance from the side walls of the chlorine vessel. Photographs taken with exposures of from one to six hours and with the vessel filled with chlorine or empty showed in no case even the slightest trace of spectrum image. On the other hand, when the spectrograph was placed behind the chlorine vessel in the path of the light beam, with a ground glass plate in front of the slit at a distance of 2 cm., a well-developable image of the spectrum was obtained even after an exposure of one second.

From these data it is easily calculable that the fraction of absorbed light energy which is reëmitted as fluorescence by dry chlorine must be considerably smaller than the upper limit of 5% determined by means of the thermopile.

V. Discussion

The results of the experiments described are these: the structure of the absorption spectrum and the total absorption of chlorine are not appreciably changed by extreme drying; only an extraordinarily small fraction of the absorbed light energy can be reëmitted as fluorescence even in very dry chlorine. On the other hand, there is little doubt as to the reality of the decrease of the Budde effect on drying chlorine. These observations of different investigators seem to contradict each other. Evidently, since fluorescence is absent and the extent of absorption is unchanged, it must be concluded that one and the same amount of light energy introduced may or may not cause a heating effect, depending only on the presence or absence of impurities in chlorine.

It is rather difficult to reconcile the new data with the theories of Weigert and others who assume that, for the primary photochemical process in chlorine, the presence of foreign molecules is necessary. The absence of fluorescence and their denial of the dissociation of "free" chlorine molecules leave no choice but the conclusion that the absorbed light energy is converted by these "free" molecules into heat, and this is in strict disagreement with the observations on the Budde effect. An assumption that the absorbed light energy is somehow stored up (in absence of water) in activated chlorine molecules, an assumption rather improbable in itself, is further decidedly disproved by experiments of Bodenstein and Taylor²¹ and of Marshall²² on the life of activated chlorine.

The difficulty in reconciling the existing data is not entirely removed by accepting the theory that the primary photochemical process in chlorine is, independently of the presence of impurities, a dissociation into atoms. Since under these circumstances the process which contributes to the warming up of the illuminated gas would be almost entirely the recombination of chlorine atoms to molecules, it must be assumed that, in absence of water molecules, this process is very slow in the gas phase and takes place almost exclusively on the dry walls of the containing vessel. Thus, the absorbed light energy will be transported to the walls and cannot cause the Budde effect on account of the large heat capacity and relatively good heat conductance of the glass walls. The experiments described give, of course, no indication as to the nature of the catalytic action of water on the rate of recombination of chlorine atoms.

A certain difficulty with the explanation of the Budde effect here ad-

²¹ Bodenstein and Taylor, *Z. Elektrochem.*, 22, 202 (1916).

²² Marshall, *J. Phys. Chem.*, 30, 757 (1926).

vanced arises from the thermodynamic consideration that in such a case the rate of thermal dissociation of chlorine molecules should also be accelerated by water vapor.

Summary

1. A brief account of theories on the nature of the primary photochemical process in chlorine has been given.

2. Earlier measurements and the data now obtained show that extreme drying of chlorine does not change appreciably either the structure of its absorption spectrum or the total amount of light energy absorbed.

3. Measurements of a possible fluorescence in dry chlorine reveal that certainly less than 5% of the absorbed light energy is reëmitted as fluorescence.

4. It has been suggested, in order to reconcile these experimental results with the known influence of moisture on the Budde effect, that chlorine (or other halogen)² is dissociated into atoms on absorption of light energy in the region of continuous absorption independently of its degree of purity; water is assumed to have a catalytic influence on the rate of recombination of the atoms and, therefore, also on the rate of thermal dissociation of chlorine molecules.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

HEATS OF ADSORPTION ON POISONED AND HEAT-TREATED CATALYSTS

BY GEORGE B. KISTIAKOWSKY,¹ EARL W. FLOSDORF, AND HUGH S. TAYLOR

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In the preceding five years the non-uniform character of the catalyst surface has been developed by quantitative studies of adsorption, reaction kinetics, poisoning and promoter action on a variety of catalysts. This differentiation in the catalytic activities of the units in the catalyst surface has permitted an experimental attack on the problem of activation at the catalyst surface, a most important step in placing the study of contact catalysis on a scientific basis and in freeing catalysis from the bane of empiricism.

Experiments by Gauger² and by Wolfenden³ on the ionization potentials of adsorbed hydrogen on hydrogenation catalysts have indicated that the hydrogen adsorbed on the more active portions of a catalyst surface may be atomic. These experiments were extended by Kistiakowsky⁴

¹ International Research Fellow.

² Gauger, *THIS JOURNAL*, **46**, 674 (1924).

³ Wolfenden, *Proc. Roy. Soc. (London)*, **110A**, 404 (1926).

⁴ Kistiakowsky, *J. Phys. Chem.*, **30**, 1356 (1926).

to ammonia-making catalysts, with the result that evidence for the presence of both atomic nitrogen and hydrogen was obtained. A series of investigations with the problem of activation as the objective is also in progress in Princeton, the heat of adsorption of the gas being the measure of activation. The work of Beebe and Taylor⁵ showed that the integral heat of adsorption of hydrogen on nickel and copper was of the order of 10,000–20,000 calories, greatly in excess of the heat of liquefaction, and variable with varying preparations of catalyst. Fryling⁶ elucidated this variable behavior by a study of promoted nickel catalysts, showing, in addition, that on active promoted catalysts the curve for the heat of adsorption with increasing adsorption gave initially low values, next a maximum and then decreasing heats of adsorption. Fryling attributed the initial rise in the curve to an activation of the adsorbed hydrogen molecules, the heat measured being a composite of a positive heat of adsorption and a negative heat of activation. Fryling assumed that, in the limit, this activation consisted in a dissociation into hydrogen atoms

As pointed out by Taylor,⁷ on the assumption of a dissociation into atoms, from the initial heat of adsorption at very low partial pressures a value of the heat of adsorption of hydrogen atoms can be deduced and hence a more penetrating analysis of the possible stages in a contact catalytic hydrogenation or dehydrogenation process may be secured. To study these limiting values of adsorption heats a more exact experimental technique has been developed⁸ which permits the measurement of the heat of adsorption of a few tenths of a cc. of gas on 100 g. of a catalyst. We have reported the results of such a study elsewhere, using a sample of reduced copper as adsorbent and both hydrogen and carbon monoxide as adsorbates. In the case of hydrogen, an active catalyst and one poisoned with oxygen were studied. The active catalyst showed a maximum in the curve similar to that reported by Fryling on nickel. Poisoning the catalyst with oxygen eliminated this maximum. In the case of carbon monoxide as adsorbate, the initial gas adsorbed showed high values, which fell as adsorption proceeded to a minimum value, the amount there adsorbed corresponding identically to the position on the hydrogen curve where a maximum was shown. The carbon monoxide heat of adsorption then showed a further increase to a maximum and subsequently a steady decrease. Kistiakowsky has shown⁹ that all these results are in agreement with a modified Langmuir theory of gas adsorption in which the surface shows varying types of "elementary spaces"

⁵ Beebe and Taylor, *THIS JOURNAL*, **46**, 43 (1924).

⁶ Fryling, *J. Phys. Chem.*, **30**, 818 (1926).

⁷ Taylor, *Proc. Roy. Soc. (London)*, **113A**, 77 (1926).

⁸ Taylor and Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927).

⁹ Kistiakowsky, *Proc. Nat. Acad. Sci.*, **13**, 1 (1927).

on some of which activation as well as adsorption of the gas molecules can occur, whereas on the remainder adsorption alone occurs.

Earlier studies of metallic catalysts¹⁰ have shown that their sensitivity to heat treatment was much more pronounced when catalytic activity instead of adsorptive capacity was used as the criterion of sensitivity. Thus, Pease showed that a 70% decrease in hydrogen adsorptive capacity and a 22% decrease in ethylene adsorptive capacity, at 1 atmosphere, were accompanied by a decrease in catalytic activity amounting to 85%. Such results pointed to the importance, for catalytic activity, of the strong or low-pressure adsorption, a conclusion which the poisoning studies abundantly confirmed. The new technique now available for measurement of heats of adsorption of small amounts of gas at very low partial pressures permits a reëxamination of the problem from the standpoint of heats of adsorption, and yields, as is shown in the following pages, abundant confirmation of this conclusion and a further development of our ideas concerning activation in its dependence on the nature of the catalyst surface. We have examined the heats of adsorption of hydrogen on an active copper catalyst and on the same catalyst after two successive reductions in activity by suitable heat treatment. For purposes of comparison we also record our earlier results with poisoned copper.

Experimental

The heats of adsorption were measured in a special glass vacuum calorimeter which has already been described in detail elsewhere.¹¹ The apparatus used in these studies was unchanged save that the dead space in the apparatus outside the calorimeter was still further reduced with the object of increasing the accuracy of the adsorption measurements. We do not, however, estimate the accuracy any higher than that previously claimed, namely, 10%; on the most important portions of the curves, below 3 cc. of adsorbed gas, we believe the accuracy is higher than this. But a 10% accuracy is adequate for all the conclusions that we shall draw from the results. In the earlier work we may have overestimated the accuracy of the measurements at the end of the curve where 80% of the gas admitted is not adsorbed. Since this part of the curve (> 8 cc. adsorbed) is not of interest in the present study, we have not pursued the measurements in this region with sufficient care to state any definitive results. The details of the measurement of heats of adsorption, extent of adsorption and of the heat capacity of the calorimeter have already been given¹² and will not be repeated here.

Catalysts Employed.—Measurements have been made on a sample of copper obtained by reduction of a high grade of copper oxide granules.

¹⁰ Pease, *THIS JOURNAL*, 45, 2296 (1923).

¹¹ Ref. 8, p. 352.

¹² Ref. 8, p. 353.

The reduction was carried out very slowly with hydrogen gas at a temperature of 160° over a period of weeks, and gave us a sample (No. 1) of high catalytic activity and adsorptive capacity. To obtain the less active preparations this catalyst was subjected subsequently to two successive heat treatments, the first at 250° for 30 hours in a vacuum, the second to 300° for a period of 8 hours. The sample after these two treatments is designated as No. 2 and No. 3 in the experimental results. On the catalyst in each state, measurements were made of the heat of adsorption of successive increments of 0.3–0.4 cc. of hydrogen up to 8 cc. adsorbed.

Experimental Results.—The experimental data thus secured are shown graphically in Figs. 1 and 2. In Fig. 1 are recorded all the experimental

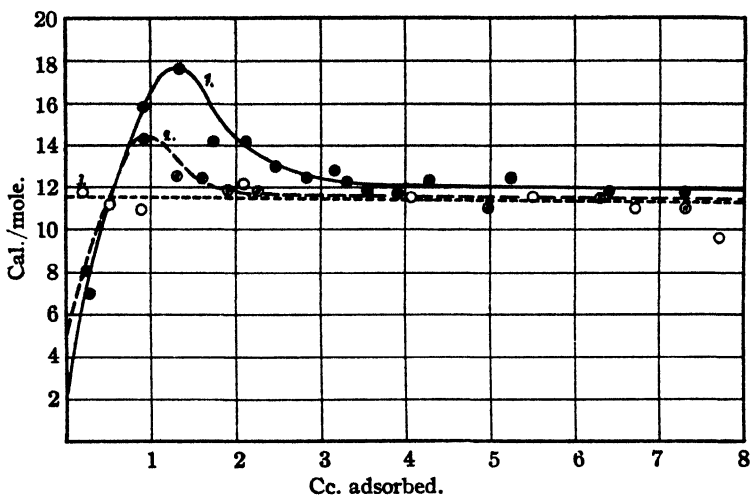


Fig. 1.—Heat treatment. 1.—● 160° ; 2.—● 250° (30 hrs.); 3.—○ 300° (8 hrs.).

data on the heats of adsorption of the catalyst in its three states of preparation. Fig. 2 records the pressure and adsorbed amount before and after the first heat treatment.

In regard to heats of adsorption, the experimental results are exactly what would be expected from our previous experience with such catalysts and from the theory of the catalytic surface developed in Princeton. The most active preparation (Fig. 1, No. 1) shows the most pronounced maximum in the curve and a maximum at a point corresponding to 1.5 cc. of adsorbed gas. The first heat treatment reduces the heat developed at the maximum and also decreases the amount adsorbed at the maximum to 1 cc. The second heat treatment eliminates all evidence of a maximum. We interpret these results as indicating in the active preparations a greater fraction of the surface capable of activating the adsorbed species,

the activation process being endothermic and, possibly, a dissociation into atoms. The heat treatment destroys these active areas on the surface preferentially.

That the destruction of these areas may be without marked influence on the *total* adsorption is evident from Fig. 2. The curves show that the pressure at which a small amount of gas is adsorbed is markedly less with the active preparation (1) than with the heat-treated catalyst (3).

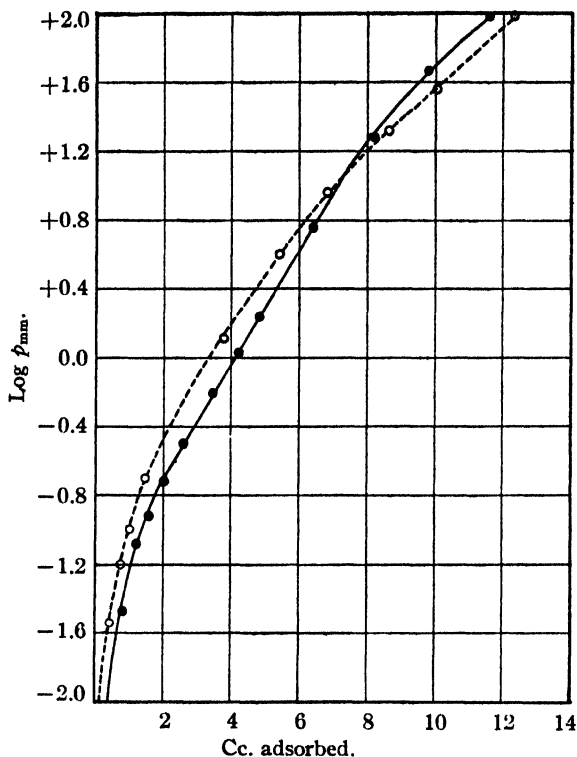


Fig. 2.—Pressure and adsorbed amount before and after heat treatment.

Heat treatment destroys the surface which adsorbs at low pressures. Beyond 8 cc. of adsorbed gas, however, the curves cross each other and, in this case at least, the heat-treated catalyst displays in the region 8–12 cc. adsorbed (20–100 mm. pressure), a higher adsorption at a given pressure. It is possible, however, that these curves might again cross each other at higher gas pressures. Our experimental set-up in this study was not suited to such measurements, but other data in this Laboratory suggest its probability. We see in such complex adsorption isotherms the best possible evidence of a surface of "variable elementary spaces,"

the distribution of which may vary widely between the extremes of most active and least active.

In Fig. 3 we record the results of an earlier study of an active copper catalyst before and after poisoning with oxygen. The active catalyst (No. 1) is seen to be in every way similar to that in Fig. 1; the poisoning with oxygen destroys the maximum in the curve and gives a curve (No. 2) which we regard as typical of adsorption without activation. This is in accord with our concept that poisons are preferentially adsorbed on the active areas.

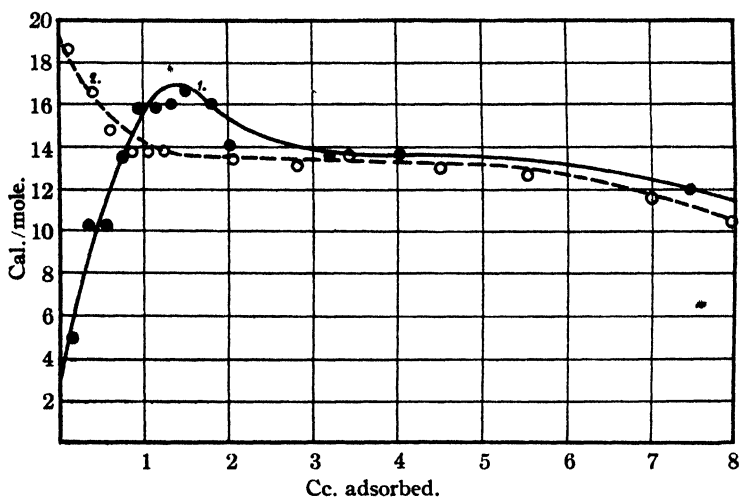


Fig 3.—Oxygen treatment.

Theoretical

A difficulty of theoretical importance in connection with these results on the heat of adsorption on active catalysts may now be stated in the hope that some suggestions may be forthcoming as to its solution. It has been pointed out to us by Professor K. Herzfeld of Johns Hopkins University that, with the active preparations, the process first occurring is one in which the decrease in internal energy is very much less than that occurring subsequently at the maximum point and beyond. There is no evidence that the entropy changes involved would cause the free energy decrease at low absorptions to be greater than those obtaining at the maximum. The problem therefore arises as to why the process with a smaller free energy decrease should occur preferentially to that in which the larger free energy decrease can take place. It is known, of course, that change in free energy is not a measure of reaction velocity in many chemical reactions. Does the same hold true in processes of adsorption?

Summary

Measurements of the heat of adsorption of hydrogen on active and heat-treated copper catalysts have been made.

The active preparations show maxima in the curves of heat of adsorption plotted against amount adsorbed.

With partially de-activated catalysts the maximum occurs when smaller amounts of gas are adsorbed. Further de-activation eliminates such maxima.

These results are in harmony with a theory of the catalytic surface with variable elementary spaces, upon the most active of which adsorption is accompanied by an endothermic activation process.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

By CHARLES A. KRAUS, E. SEATON CARNEY AND WARREN C. JOHNSON

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According to Kraus and Lucasse¹ the density of a concentrated solution of sodium or potassium in liquid ammonia is markedly lower than that of either of its components, which shows that the process of solution of these metals is accompanied by a large increase in volume. Forney² investigated the density of solutions of sodium in liquid ammonia at higher concentrations, using for this purpose a specially designed spring balance. This method, however, did not prove sufficiently sensitive to admit of accurate determination of the volume change. Since these solutions are very exceptional in their behavior, it was thought worth while to develop a method whereby their density could be determined with a relatively high degree of accuracy. An apparatus was therefore designed whereby the density was measured directly by means of a Westphal balance.

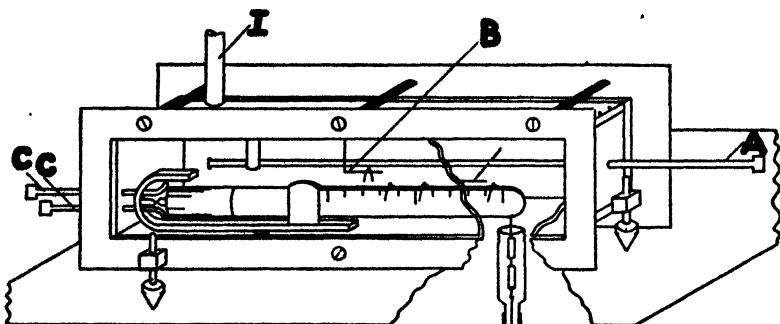
Apparatus and Procedure

The chief difficulty encountered in determining the density of solutions of the alkali metals in liquid ammonia is due to their extreme reactivity toward oxygen and moisture. This was overcome by maintaining an atmosphere of hydrogen over the solutions during the course of the measurements. The essential features of the apparatus are shown in outline in Fig. 1. The balance, which was equipped with suitable clamping and leveling devices, was placed in a sealed case provided with plate glass windows on opposite sides. Special riders were constructed of inverted "U" form, carrying a loop at the top. The riders were manipulated

¹ (a) Kraus and Lucasse, *THIS JOURNAL*, **43**, 2538 (1921); (b) *ibid.*, **44**, 1941 (1922).

² Forney, *Thesis*, Clark University, 1923.

from without the case by means of a rider carrier A. A hook B was



provided within the case on which the riders were placed when not in use. The beam could be fixed in position by means of the clamps CC. The balance case was connected to the density tube D by means of a short length of rubber tubing E. A special bob F was constructed of Pyrex glass and adjusted to have a volume of 5.000 cc. at -33.8° , the temperature at which the density measurements were carried out. The density of the solutions could thus be read directly in terms of the position of the riders on the beam. The beam was connected to the bob by means of a silk thread G, which passed through the rubber tube E, and which, in turn, was connected to a fine platinum wire H attached to the bob. During the weighing operations, the density tube D, as well as the balance case, was filled with pure hydrogen at a pressure slightly above that of the atmosphere. In general, a slow stream of hydrogen was maintained through the upper portion of the density tube and the case and out through the tube I, which was connected with a mercury trap, not shown in the figure. Except during the weighings, connection between the

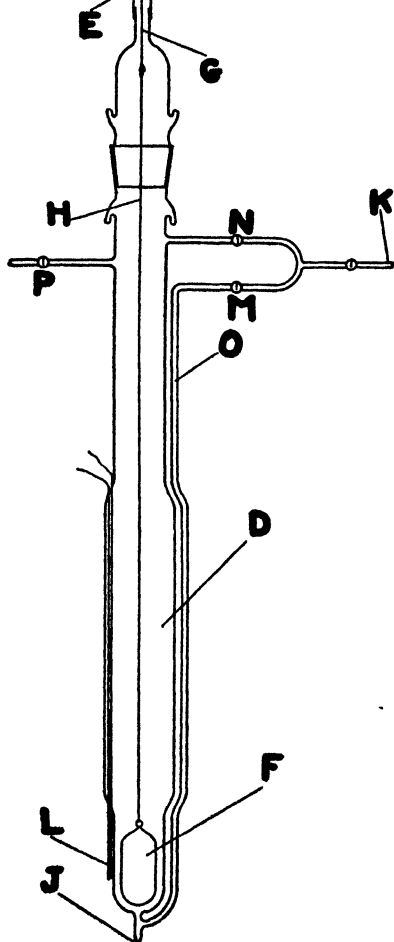


Fig. 1.

balance case and the density tube was shut off by compressing the rubber tube E with a small screw clamp.

Sodium was introduced into the bottom of the density tube through a fine capillary by the method of Kraus and Lucasse,¹ the tube being sealed off at J on completion of this operation. The tube K was connected with a source of pure ammonia, a high-vacuum pump, a source of pure hydrogen and a Toepler pump. The procedure used in introducing liquid ammonia into the tube D was similar to that described by Kraus and Lucasse.¹ The volume of the solvent was measured, prior to introduction, by means of pipet cells having a volume of from 2 to 10 cc. and graduated in 0.01 cc.

In making a series of density determinations, the following procedure was employed. After introducing the sodium, the density tube was thoroughly evacuated. It was then surrounded by a bath of ammonia (in a Dewar tube) boiling freely under the pressure of the atmosphere. An electric current was passed through the small nichrome wire coil L for the purpose of maintaining constant ebullition. Liquid ammonia, whose volume had been measured in the pipet cells, was then condensed in the tube D, the ammonia vapor passing through the tubes K and O and the stopcock M. The solution was thus stirred by the vapor passing through it. The stopcock P connected the density tube with the external atmosphere through a mercury trap and wash bottle in which any ammonia carried over was absorbed and later determined by titration. After condensing the ammonia in the density tube, a stream of hydrogen was passed through the stopcock M and tube O for the purpose of stirring the solution until equilibrium was established. Any ammonia carried over with the escaping hydrogen was absorbed in the wash bottle already mentioned and later determined by titration. The screw clamp attached to E was then removed, the balance beam was set free and the density read by means of the Westphal balance. The clamp was then replaced and the hydrogen present in the density tube, together with a small quantity of ammonia which varied with the concentration of the solution, was removed by means of a Toepler pump. The ammonia carried over in this process was absorbed in water and determined by titration. The stopcock N was used for the purpose of equalizing the pressure between the density tube and the auxiliary tube O.

After having removed the hydrogen from the density tube, another measured quantity of ammonia was introduced and the density determined as before. The procedure, as above described, was repeated until the limit of capacity of the density tube was reached.

The ammonia present in the tube was then evaporated and the last trace removed by means of a high-vacuum pump. The tube J was broken off near the tip and the sodium dissolved in a mixture of 50% of absolute alcohol and ether. When the metal was completely dissolved, the solution was allowed to run into a large platinum dish and sulfuric acid was added until it was neutral or slightly acid. The solvent was then evaporated, an excess of acid was added and the sodium finally determined as sodium sulfate.

In order to determine the volume change accompanying the formation of the saturated sodium solution from its components, it was necessary to make a precise determination of the concentration of this solution. This was done by the method of Kraus and Johnson,² a detailed description of which need not be repeated here. It consists essentially

² Kraus and Johnson, *THIS JOURNAL*, 47, 725 (1925).

in measuring the equilibrium pressure for a series of mixtures of sodium and ammonia of known composition. So long as sodium is present in excess, the pressure remains fixed, but as soon as the amount of ammonia is in excess of that necessary for complete solution of the sodium, a rapid rise in pressure occurs. By graphical means the point corresponding to the saturated solution can be evaluated with considerable precision. The pressure measurements were extended to fairly dilute solutions in order to obtain the data necessary for correcting the concentrations, in the density determinations, for ammonia present in the vapor phase.

Results

The density values as obtained are presented in Table I, in which the weight of ammonia in the solution is given in the first column, the number of moles of ammonia per atom of sodium in the second column, the density of the solution in the third column and the volume change per atom of sodium, ΔV , in the last column. The volume change is calculated by means of the equation

$$\Delta V = \frac{N \times 17.032 + 22.997}{D_s} - \left(\frac{N \times 17.032}{D_{NH_3}} + \frac{22.997}{D_{Na}} \right)$$

where N is the number of moles of ammonia per atom of sodium, D_s is the density of sodium at the temperature of the solution and D_{NH_3} is the density of pure ammonia at the same temperature. The reduced barometric reading during the experiment was 742.25 mm. of mercury, which corresponds to a temperature of -33.8° for the boiling point of liquid ammonia.⁴ The density of pure ammonia at this temperature is 0.6824⁵ and that of sodium 0.9805. The latter value was obtained by

TABLE I

DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT DIFFERENT CONCENTRATIONS

$t = -33.8^\circ$. Sodium sulfate = 6.9190 g. \approx 2.2402 g. of sodium

NH ₃ , g.	NH ₃ /Na	Density	V
7.562	5.48	0.5782	40.96
11.160	6.731	.5888	42.26
14.700	8.867	.6044	43.15
18.278	11.025	.6163	43.37
21.713	13.097	.6251	43.29
25.271	15.243	.6322	43.13
28.857	17.406	.6376	43.13
32.544	19.630	.6423	42.93
36.054	21.747	.6462	42.54
39.901	24.072	.6494	42.48
45.200	27.263	.6535	41.82
54.061	32.608	.6582	41.40

⁴ Cragoe, Meyers and Taylor, Bureau of Standards, *Scientific Papers*, No. 369, p. 33, 1920.

⁵ Cragoe and Harper, *ibid.*, No. 420, p. 313, 1921.

interpolating data due to Dewar at 17 and -182.6° ,⁶ and combining this with a value determined by Richards and Brink⁷ at 20° .

TABLE II

VAPOR PRESSURE OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT DIFFERENT CONCENTRATIONS AT -33°

Series 1						
Conc. NH_3/Na	4.824	5.424	5.566	5.711	5.774	5.869
Press., mm.	405.0	398.0	421.0	445.0	461.0	469.0
Conc. NH_3/Na	5.932	6.051	6.146	6.295	6.700	7.243
Press., mm.	483.5	493.0	516.0	533.5	577.5	623.6
Conc. NH_3/Na	7.812	8.383	8.934	9.521	10.745	13.561
Press., mm.	656.5	686.5	707.5	732.2	745.5	769.0
Series 2						
Conc. NH_3/Na	2.839	3.995	4.532	5.097	5.461	5.602
Press., mm.	397.0	397.0	401.0	403.0	403.0	431.5
Conc. NH_3/Na	6.008	6.469	6.910	7.314	7.922	8.367
Press., mm.	486.0	544.5	592.5	625.0	661.5	681.5

In Table II are given the values of the equilibrium pressures as measured for solutions of sodium in liquid ammonia at various concentrations, including saturated solutions.

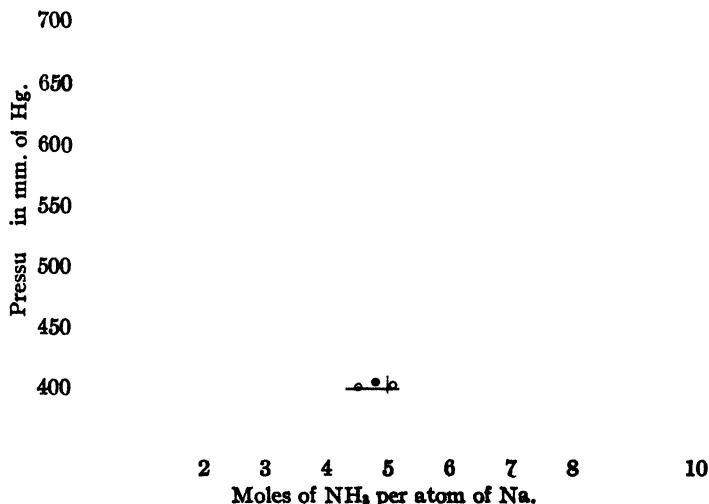


Fig. 2.

These results presented in Table II are shown graphically in Fig. 2, where pressures are plotted as ordinates against moles of ammonia per

⁶ Dewar, *Chem. News*, 85, 277 (1902).

⁷ Richards and Brink, *THIS JOURNAL*, 29, 117 (1907).

atom of sodium as abscissas. Points of Series 1 are represented by combined crosses and circles and of Series 2 by crosses.

From the plot the composition of the saturated solution of sodium in liquid ammonia was found to be 5.48 moles of ammonia per atom of sodium.

Discussion

The density of solutions of sodium in liquid ammonia is shown as a function of the concentration in Fig. 3, in which densities are plotted as ordinates. In Curve 2, the number of moles of ammonia per atom of sodium are plotted as abscissas, while in Curve 1 the number of atoms of sodium per mole of ammonia are correspondingly plotted. In Fig. 4 values of ΔV are plotted as a function of the concentration expressed in moles of ammonia per atom of sodium.

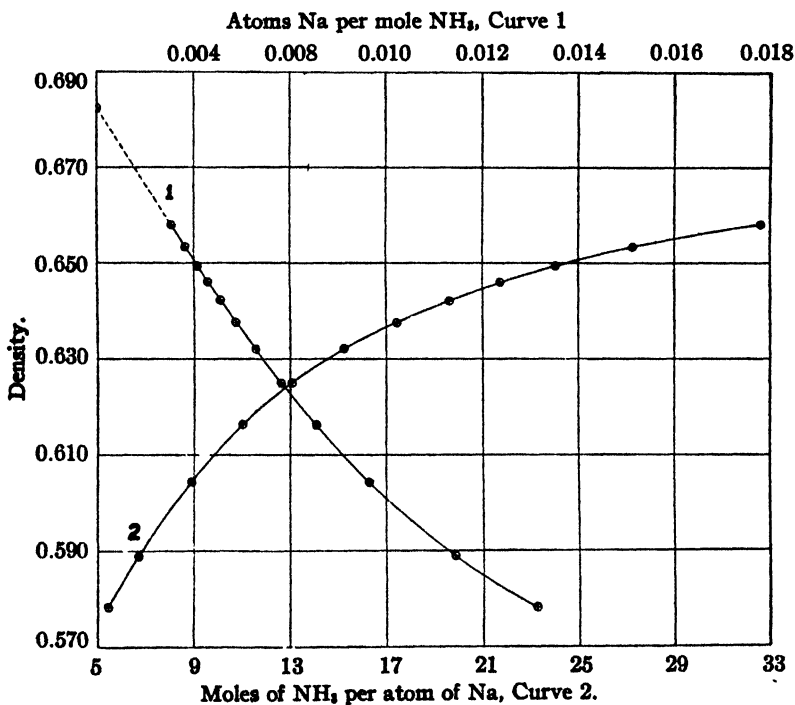


Fig. 3.

The relative values of the density are consistent with one another within less than two units in the fourth place. This is well illustrated by the ΔV curve (Fig. 4), which is quite sensitive to errors in the density values. The maximum deviation of the values of ΔV , as determined, from those of the smooth curve, as drawn, lies well within an error limit of two units in the fourth place in the value of the density.

The density of the saturated solution has a value of 0.5782 as against 0.6824 for pure ammonia and 0.9805 for sodium. From the determined concentration of the saturated solution, the volume change accompanying the formation of this solution from its components is found to be 40.96 cc. per atom of sodium. With decreasing concentration, the value of ΔV increases, reaching a maximum of 43.37 cc. per atom of sodium at a concentration of 11.25 moles of ammonia per atom of sodium. Beyond this concentration, the value of ΔV diminishes slowly. Judging by the form of Curve 2 (Fig. 3), as well as by that of the ΔV curve (Fig. 4), it is probable that, with decreasing concentrations, the value of ΔV approaches a constant value somewhat less than 40 cc. per atom of sodium. The

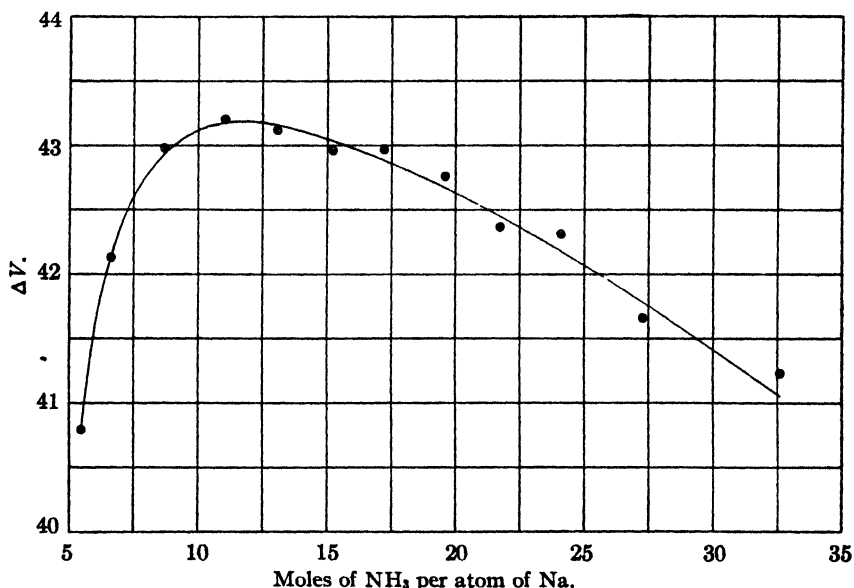


Fig. 4.

most dilute solution measured contained 32.6 moles of ammonia per atom of sodium with a density of 0.6582, which corresponds to a volume concentration of 1.138 *N*. At this concentration the solutions are rapidly approaching a constant condition as regards the state of the dissolved substance.

The volume change accompanying the formation of these solutions is a striking fact. It amounts to almost twice the original volume of the sodium. The heat effect accompanying the solution of sodium in liquid ammonia is inconsiderable. About 1500 calories are absorbed per atom of sodium and the value diminishes with increasing concentration.⁸ If we bear in mind the fact that, in these solutions, sodium is present as a

⁸ This value is based on measurements carried out by Mr. J. A. Ridderhof in this Laboratory. The detailed results will be published later.

normal sodium ion, we must ascribe the volume change chiefly to the electron which, freed from the constraints under which it exists in the solid metal, occupies a relatively large volume in the solution. In no other case heretofore investigated, either in processes of solution or of compound formation, has a volume change of this magnitude been observed. It is known that the electron in liquid ammonia solution at higher concentrations is free to move as it is in metals. Since we have no adequate conception of the state of the electron in metals, we are unable to draw any definite conclusions regarding its state in liquid ammonia. However, it may be safely concluded that the electron is not combined with the sodium ion and that at low concentrations, at any rate, the electron is associated with ammonia molecules.

The peculiar form of the ΔV curve at higher concentrations cannot be accounted for at this time. It is known that in concentrated solutions of the alkali metals in liquid ammonia, many properties exhibit singularities. The electrical conductance, for example, undergoes a tremendous increase in value with concentration as was shown by Kraus and Lucasse, while the temperature coefficient of the conductance exhibits a sharp maximum in the neighborhood of normal concentration.¹ The concentrations at which these singularities occur differ in the case of different properties.

Summary

The density of solutions of sodium in liquid ammonia has been determined at -33.8° at concentrations ranging from 32.6 moles per atom of sodium up to the saturation point.

The density of these solutions is lower than that of either constituent.

From the density values the increase in volume accompanying the solution of sodium in liquid ammonia has been calculated. The volume increase amounts to 40.96 cc. for a saturated solution and increases with increasing dilution to a maximum of 43.14 cc. for a solution containing 11.2 moles of ammonia per atom of sodium. On further dilution the value gradually diminishes and apparently approaches a limiting value in the neighborhood of 40 cc. At -33.8° the saturated solution of sodium in ammonia contains 5.48 moles of ammonia per atom of sodium.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IDAHO]

DIPHENYLAMINE AS A QUALITATIVE REAGENT FOR ZINC

BY W. H. CONE AND L. C. CADY

RECEIVED JULY 5, 1927

PUBLISHED SEPTEMBER 2, 1927

The qualitative separation of zinc from chromium by the systems of analysis in general use requires considerable time. The production of the green cobalt zincate used as a confirmatory test is dependent upon the comparative amounts of cobalt nitrate and zinc present. Properly adjusting these amounts offers considerable difficulty to inexperienced analysts. The employment of diphenylamine and diphenylbenzidine as indicators in the titration of zinc¹ suggested their utilization in a qualitative test for zinc. A 0.5% solution of potassium ferricyanide and one gram of diphenylamine dissolved in 100 cc. of glacial acetic acid are the solutions used in this test.

Method

After the separation of the iron and aluminum groups by sodium hydroxide and sodium peroxide, the filtrate containing the aluminum group is acidified with hydrochloric acid, ammonium chloride is added, and the aluminum precipitated with ammonium hydroxide. The filtrate containing the chromium and zinc is acidified with acetic acid and divided into two equal parts. One part is tested for chromium and the other for zinc. To the part to be tested for zinc, five drops of the diphenylamine acetate solution and 5 cc. of the 0.5% potassium ferricyanide solution are added. The immediate appearance of a dark brown, green or purplish-black turbidity indicates the presence of zinc.

To test for any zinc that might be carried over into the iron group, the sulfides of zinc, cobalt and nickel are stirred for a few minutes with cold, dilute hydrochloric acid and filtered. The hydrochloric acid solution is boiled until all of the hydrogen sulfide is expelled, sodium hydroxide is added to alkalinity, the solution cooled and one gram of sodium peroxide added in small portions, with stirring. The mixture is boiled to decompose the excess sodium peroxide, cooled and filtered. The filtrate containing the zinc is acidified with acetic acid and the diphenylamine acetate and potassium ferricyanide are added as above.

Knop² states that in the absence of iron salts no coloration is produced by bichromate in a dilute solution of diphenylamine sulfate. This was found to be true only when the amount of bichromate present was small, less than .05 mg. per cc., a blue color being produced immediately if the concentration of bichromate was .05 mg. per cc. or greater. By using diphenylamine acetate instead of diphenylamine sulfate no color

¹ Cone and Cady, *THIS JOURNAL*, 49, 356 (1927).

² Knop, *ibid.*, 46, 263 (1924).

was produced unless the amount of chromium present was over 10 mg. of potassium bichromate per cc. of solution. This makes it possible to test for zinc in the presence of bichromate.

The color produced is dependent upon the relative amounts of zinc and chromium present. If much chromium is present the color will vary from a brown to a brownish-black. If chromium is absent the color will vary from a green to a purplish-black, depending on the amount of zinc present. The presence of chromium may cause the solution to turn dark on long standing even in the absence of zinc.

The following table shows the colors produced by varying the amounts of zinc and bichromate. Five cc. of potassium ferricyanide solution and five drops of diphenylamine acetate solution were used in each test.

TABLE I
COLORS PRODUCED BY VARYING MIXTURES OF ZINC AND BICHROMATE IONS

Mg. Zn per cc.	Mg. $K_2Cr_2O_7$ per cc.	Color produced
0.02	None	Pale green
.02	0.5	Greenish-yellow
.02	5.0	Brownish turbidity
.04	None	Greenish-black
.04	0.5	Greenish-brown
.04	5.0	Brown
.2	None	Blue violet
.2	0.5	Black
.2	5.0	Black

All the colors in the above table were quite distinct except when 0.02 mg. of zinc and 5.0 mg. of potassium bichromate were used, but even then there was a marked turbidity as compared with a potassium bichromate solution treated in the same manner.

A small amount of zinc ferrocyanide is always precipitated, due to the reduction of some ferricyanide to ferrocyanide by the diphenylamine. However, under the conditions prevailing any such zinc ferrocyanide formed is always dark colored on settling. Diphenylamine was used in preference to diphenylbenzidine as it is much cheaper and gives equally good results.

Summary

1. The use of diphenylamine as a qualitative reagent for zinc shortens the time required for the analysis of the aluminum and iron groups.
2. The test is more delicate than the cobalt zincate test.
3. The amount of zinc present may be estimated by the depth of the color produced.

MOSCOW, IDAHO

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE COEFFICIENT OF SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE

BY ETHEL M. TERRY¹ AND JULIUS STIEGLITZ²

RECEIVED JULY 5, 1927

PUBLISHED SEPTEMBER 2, 1927

An accurate determination of the coefficient of saponification of ethyl acetate by sodium hydroxide in mixtures of about one-hundredth molar concentration was undertaken as a part of the studies of catalysis carried out in this Laboratory under the direction of one of us.

The general method of work was not new. However, each detail of operation was carried out with greater precision than had been attempted before. Accurately measured volumes of reaction mixture were discharged at noted times into measured quantities of acid, calculated to be slightly in excess of that needed to neutralize the sodium hydroxide in the samples taken. The excess acid was then titrated and the concentration of sodium hydroxide calculated from the data thus obtained. The critical points in the success of the work were, first, the establishment of a suitable technique for handling the solutions without contamination with carbon dioxide of the air, and, second, the design of an apparatus which permitted very rapid discharge of accurately measured volumes of reaction mixture without exposure of the main solution to air. Details of the method and the preparation of materials will be found in Part II of this paper.

¹ The work herewith presented was completed in 1913 and embodied in the dissertation of one of us in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

² The present investigation was designed to lay the foundation for a critical study by exact methods of catalysis by alkalies as affected by ionization, by the presence of salts and by other factors. The further development of the study was carried out under the direction of Dr. Terry, acting at first as my research assistant but later acting independently. The results of these later investigations will be published by Dr. Terry and her collaborators as follows:

Influence of Added Salts on the Velocity of Saponification of Ethyl Acetate by Sodium Hydroxide. I, by S. D. Wilson (1916); II, by Ralph E. Nelson (1918).

The Coefficient of Saponification of Methyl Acetate by Sodium Hydroxide, by W. T. Gooch (1918).

Influence of Light on the Saponification of Ethyl and Methyl Acetate by Sodium Hydroxide, by W. T. Gooch (1918).

The Saponification of Ethyl Formate by Ammonium Hydroxide in the Presence of Ammonium Salts, by E. N. Roberts.

The delay in publication has been altogether due to pressure of work on the present writer. Dr. Terry kindly consented finally to undertake the critical study of the results as a whole in the light of more recent knowledge of the nature of solutions and has developed a theory covering the data obtained under a wide range of experimental conditions.

This theory will be presented by Dr. Terry in another paper.—Julius Stieglitz.

The coefficient of the reaction was calculated by the well-known bi-molecular reaction equation, $dx/dt = K(A - X)(E - X)$. K is the coefficient; A represents the initial concentration (moles per liter of solution) of sodium hydroxide; E , the initial concentration of ester; X is the concentration or moles per liter of solution of alkali or ester used in the reaction at the moment considered; t is the time in minutes. The integrated form for the interval between two observed times, t_1 and t_2 , is

$$K = \frac{2.303}{(A - E)(t_2 - t_1)} \log \frac{(E - X_1)(A - X_2)}{(A - X_1)(E - X_2)}$$

TABLE I
A REPRESENTATIVE EXPERIMENT

Initial concentration of sodium hydroxide = 0.01001 N ; initial concentration of ester = 0.008072 N .

Time, min.	Temp., °C.	Concn. of NaOH	K , if $t_1 = 2.27$	K , if $t_1 = 3.01$
2.27	24.915	0.008934
3.01	24.920	.008630
5.85007669	6.71	6.71
6.83	24.915	.007392	6.72	6.71
8.02	24.920	.007085	6.72	6.71
8.92	24.920	.006872	6.70	6.69
10.05	24.920	.006632	6.68	6.67
10.96	24.920	.006441	6.71	6.70
11.93	24.920	.006258	6.71	6.70

Average temperature of this experiment, 24.92°. Average = 6.70 for 24.91°, the temperature of series of experiments.

TABLE II
SUMMARY OF EXPERIMENTS

Exp.	NaOH, moles per liter	Ethyl acetate, moles per liter	Temp. = 24.91°	Temp. = 25.11°
1	0.009984	0.008023	6.71	...
2	.009984	.007964	6.70	...
3	.009984	.007983	6.68	...
4	.009984	.008168	6.71	...
5	.009984	.008073	6.70	...
6	.009984	.008064	6.695	...
7	.009984	.007940	6.715	...
8	.009986	.008014	6.705	...
9	.009986	.008117	6.71	...
10	.009983	.007990	6.70	...
11	.009986	.007989	6.70	...
Average 6.70				
12	.009984	.008055	..	6.805
13	.009984	.008106	..	6.780
14	.009984	.008055	..	6.790
15	.009986	.008112	..	6.820
17	.009986	.008165	..	6.790

Average 6.79

Change in reaction coefficient for rise of $0.20^\circ = 0.09$.

Therefore, coefficient for $25.00^\circ = 6.75$.

The average temperature (approximately 25°) per minute during the measurement of the reaction was computed and called the temperature of reaction. Then measurements were made at two-tenths of a degree higher temperature and the coefficient determined. From this it was estimated that the coefficient increased by 0.0045 for a rise of 0.01°. The results of each experiment were then corrected for difference in temperature from 24.91 in the first series or 25.11 in the second series. Data from a typical experiment are given in Table I. A summary of experiments appears in Table II.

When further studies were made on the saponification of ethyl acetate, these measurements were repeated from time to time as a means of ascertaining that experimental conditions were being kept constant. A summary of the data of various workers is given in Table III, together with a statement of the number of experiments represented, and the average and the maximum deviation of values from the average for the coefficient at 25.00° by each worker.

TABLE III

SUMMARY OF VALUES FOUND BY DIFFERENT WORKERS IN THIS LABORATORY (REF. 1)

Observer	No. of expts.	Av. coeff.	Av. dev. from mean, %	Max. dev., %
Terry (1913)	17	6.75	0.06	0.4
Wilson (1916)	8	6.76	.04	.3
Gooch (1918)	8	6.77	.2	.6

From Table III it will be seen that the results were reproducible to within one-third of one per cent. However, the error in the evaluation of the coefficient was three-quarters of one per cent. because of limitations of accuracy of measurement of time and of volume of solutions as will be explained in Part II.

TABLE IV

SUMMARY OF OLDER WORK

Experimenter	NaOH	Ethyl acetate	Temp.	Coeff., K	Coeff., at 25°
Warder ³	0.02	0.02	25	6.4	6.4
Ostwald ⁴	.025	.025	25	6.48	6.48
Arrhenius ⁵	.025	.025	24.7	6.59	6.77
	.0125	.0125	24.7	6.48	6.66
	.00625	.00625	24.7	6.58	6.77
Cohen ⁶	.025	.025	25	6.86	6.86
Reicher ⁷	0.02-03	.016-024	24.22	6.15	6.36
Crichton ⁸	.01	.01	24.85	6.47	6.84

³ Warder, *Ber.*, 14, 1361-65 (1881). Coefficient at 25° is calculated from his temperature coefficient.

⁴ Ostwald, *J. prakt. Chem.*, 35, 112 (1887); also Ref. 5, note 4.

⁵ Arrhenius, *Z. physik. Chem.*, 1, 110 (1887).

⁶ Cohen, *Proc. Acad. Sci. Amsterdam*, 2, 618 (1900).

⁷ Reicher, *Ann.*, 228, 257 (1885).

⁸ Crichton, *Proc. Roy. Soc. (London)*, 78, 157 (1907).

The value 6.76 may, therefore, be taken for the coefficient at 25° with the certainty that the error is less than three-fourths of one per cent.

The necessity of the above work will become apparent from Table IV, which contains a summary of the results of previous workers. Except where otherwise indicated, the temperature coefficient of 0.0045 for 0.01° change was used in estimating the reaction coefficient at 25°. A divergence of 7.5 per cent. will be observed between the highest and lowest results.

Part II. Experimental Detail

All vessels were filled with carbon dioxide-free air before they were used. When a transfer of solution was made, the opening of the flask which received the liquid was plugged lightly with cotton in the free space between buret tip or discharge tip and neck, etc. Only pure (carbon dioxide-free) air was allowed to enter the vessel from which the discharge was made.

Solutions were made with water of not greater than 1×10^{-6} mho conductance. All solutions, whether acid or alkaline, were handled as described above.

Sodium hydroxide was made by plunging freshly cut pieces of sodium under water at 0°. Each piece was held in a copper gauze basket, which was withdrawn as soon as the reaction was over. An atmosphere of carbon dioxide-free nitrogen was maintained over the water during the operation. Tests showed that no contamination of the solution by the copper basket took place.

Hydrochloric acid used in the titrations was standardized by the silver chloride method.

Ethyl acetate was made in four different ways: action of (1) acetyl chloride on alcohol; (2) acetic acid on alcohol, catalyzed by hydrochloric acid; (3) acetic anhydride on alcohol; and (4) alcohol, sulfuric acid and acetic acid, as described by Wade and Merriman.⁹ In each case the final purity of the product was tested by saponifying a weighed sample of ester and titrating the unused alkali. A fifth sample was obtained from Kahlbaum and purified by fractional distillation.

The indicator used in the titrations was phenolphthalein. It was purified by the method of McCoy¹⁰ and dissolved in carbon dioxide-free alcohol.

The end-point of the alkalimetric titrations was taken as the first faint color of the indicator. This is reported to represent a hydrogen-ion concentration close to 10^{-8} .¹¹ The accurate observation of this color required white light and a true white background. A so-called daylight lamp was found to be a great help in securing the correct conditions.

⁹ Wade and Merriman, *J. Chem. Soc.*, 101, 2429 (1912).

¹⁰ McCoy, *Am. Chem. J.*, 31, 507 (1904).

¹¹ Clark, "The Determination of the Concentration of Hydrogen Ion," Williams and Wilkins, Baltimore, 1922, p. 301.

Air for filling containers for samples to be titrated was purified by filtration through moist soda lime about one meter in length. That used for the larger containers was stored over molar sodium hydroxide usually about 24 hours prior to use. Test of the purity of the air was made by titrating 50 cc. of water which had been shaken with a 500cc. sample of the air. One drop of 0.01 *N* baryta was sufficient to bring the color change of the indicator, phenolphthalein, if the air was of acceptable purity.

Apparatus.—The apparatus was simply an improvement of Reicher's device.⁷ It can best be described by reference to Fig. 1. A is a container for the reaction mixture.

B is a removable head. It consists of a rubber stopper, backed with a monel metal plate fitted with lugs which permitted rapid clamping into place. Through the stopper passed a Beckmann thermometer, an air outlet tube with the stopcock 1 and the discharge tube C. A mercury pipet D was connected to A through stopcock 2. Mercury was fed into the pipet through the stopcock 3 from a reservoir under pressure from water from the hydrant. The flow of mercury to A from D was controlled by stopcock 3. The mercury pipet had two graduated scales at *n* and *m*, as indicated, and the volumes between the various graduations were known. At the start of the experiment the connections from C to A were filled with mercury as shown. All rubber-to-glass or glass-to-metal joints were made with de Khotinsky cement.

The apparatus was contained in a de Khotinsky thermostat, regulated with a constancy of 0.01°. The thermometers used were standardized by comparison with two Baudin thermometers.

Manipulation of Apparatus.—When a mixture of sodium hydroxide and ethyl acetate solution had been made in A, the top was clamped into place and mercury was forced into A to displace the air. The operator closed the discharge tube with the left hand and finally closed the air tube after the exclusion of air had been completed. A container holding the necessary acid was then put in place before the tube C and mercury discharged from the pipet into A, thus displacing a sample of the same volume from A into the receiver. The discharge occupied about five seconds and it was usually possible to collect the first sample two minutes after the original mixture had been made. The volume of the discharge, about 100 cc., was known from the levels of the mercury in *m* at the start and in *n* at the end of the discharge. The time of half discharge was observed and also the temperature of the mixture.

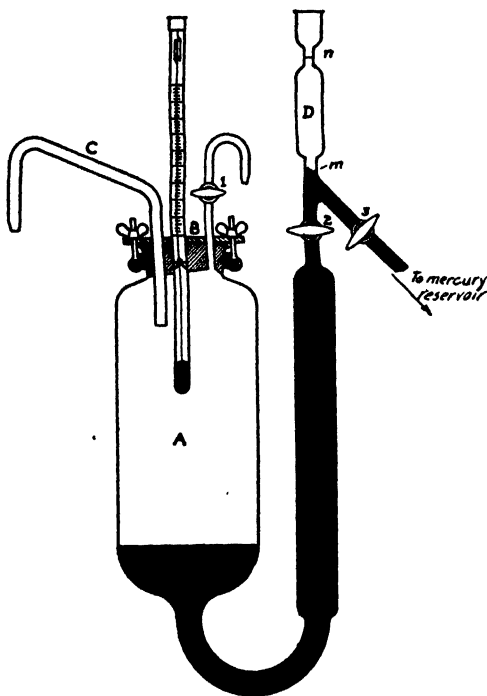


Fig. 1.

Analysis of Samples.—As has been stated, samples were discharged into a known quantity of acid. Before titrating the excess acid the mixture was frozen and allowed to thaw during the titration at such a rate that the last of the ice melted just before the titration was completed. From the data of titration, the concentration of sodium hydroxide at the time of discharge was calculated. The alkali was always greater in concentration than the ester. Hence, the final concentration of alkali gave the difference in concentration of alkali and ester, and thus the calculation of the concentration of ester at the time of each discharge was made possible.

Accuracy of Results.—Rigid adherence to an established technique permitted the reproduction of results to within one-third of one per cent. There were, however, certain limitations of the absolute accuracy of the results. When carbon dioxide is rigorously excluded from titrations of 0.01 *N* sodium hydroxide solutions, they may be completed with an accuracy limited only by the correct choice of indicator and the reading error of the buret. If allowance is made for the error in measurement in volumes not only of samples of reaction mixture, but also of the acid used to neutralize the sample and of the alkali used in completing the titration, then an error of 0.10 cc. will be seen to be the maximum probable. If the measurements had not been carried out with a strict observance of the conditions of calibration of the apparatus used, so great an accuracy could not be claimed. An error of 0.10 cc. was of no importance in the measurements made during the progress of the reaction. However, at the end of the reaction the titration results were equivalent to only 20–30 cc. of reagent, so that this error could then cause an error of one-half of one per cent. in the evaluation of $(A - E)$ and, therefore, of the coefficient.

Another source of error was the determination of the time of half discharge. This was observed by cooperation of two persons, one watching the descent of the mercury and the other watching the stopwatch in the usual way. The error could not have been greater than two-fifths of a second and the net effect on the accuracy of the determination of the coefficient was not over one-fourth of one per cent. Since the accuracy of the stopwatch was checked by comparison with a standard timepiece with which it agreed within five seconds over a period of 24 hours, no other error was introduced.

Therefore, the absolute accuracy of the value of the coefficient of the saponification may be taken to be better than three-fourths of one per cent.

Summary

Measurements were made of the velocity of saponification of ethyl acetate by sodium hydroxide in aqueous solution in mixtures of approximately one-hundredth normal concentration. The coefficient of the reaction calculated on the basis of the bimolecular equation is 6.76 for 25.00° and is accurate to three-fourths of one per cent. A change of 0.10° in temperature alters the coefficient by 0.045. The technique established

has been the basis of forthcoming studies on different aspects of the problem of catalysis of ester saponification in water solution.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE EPPLEY LABORATORY]

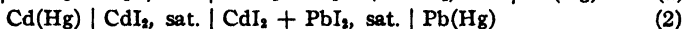
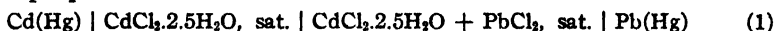
CELLS OF THE STANDARD CELL TYPE WITH LOW ELECTROMOTIVE FORCES

By WARREN C. VOEBURGH

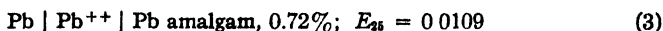
RECEIVED JULY 15, 1927

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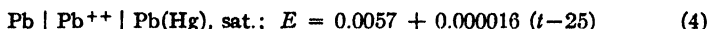
A standard cell with a low electromotive force would have some advantages over the ordinary standard cell in the measurement of small electromotive forces. Obata¹ has investigated the possibility of using for this purpose the cells



Taylor and Perrott² set up and measured some cells similar to Cells 1 and 2, the only difference being that they used an unsaturated lead amalgam, 0.72% lead. By combining the electromotive forces of their cells with the electromotive force of the cell



which was measured by Brönsted,³ and that of the cell



which was measured by Gerke⁴ the electromotive forces of Cells 1 and 2 can be calculated. For Cell 1 at 25° the value 0.1432 volt is obtained from the results of Taylor and Perrott, while Obata found 0.1408 volt. Similarly for Cell 2 at 25° the value 0.1020 volt is obtained from the results of Taylor and Perrott, while Obata found 0.0996 volt. Thus, there is a difference of about 2.2 mv. between the results of Taylor and Perrott and those of Obata for both cells.

Van Ginneken and Kruyt⁵ have given as the requirement for a standard cell that, with temperature and pressure constant, both electrode systems must be invariant systems of the same components. The cells of Taylor and Perrott did not conform to this specification because the lead amalgam was not a two phase amalgam. One electrode system, therefore, was not an invariant system. Also, the other electrode system contained no lead. The cells of Obata were not true standard cells because the cadmium-amalgam electrode system contained no lead.

¹ Obata, *Proc. Phys. Math. Soc. Japan* [3], 3, 64, 136 (1921).

² Taylor and Perrott, *THIS JOURNAL*, 43, 486 (1921).

³ Brönsted, *Z. physik. Chem.*, 56, 668 (1906).

⁴ Gerke, *THIS JOURNAL*, 44, 1697 (1922).

⁵ Van Ginneken and Kruyt, *Z. physik. Chem.*, 77, 744 (1911).

To make Cells 1 and 2 into true standard cells, according to the specification of Van Ginneken and Kruyt, the cadmium amalgam must be replaced by an amalgam saturated with both cadmium and lead. The system cadmium-lead-mercury has been studied by Kremann, Prammer and Helly,⁶ who found that within a certain range of compositions the cadmium activity was constant. The author⁷ has tried replacing the cadmium amalgam of the Weston standard cell with a cadmium-lead amalgam having a composition within the constant cadmium activity range. The cells were as reproducible as true Weston cells and had an electromotive force 1.13 mv. higher at 25°.

The work described below was undertaken to study the effect of replacing the cadmium amalgam of Cells 1 and 2 with cadmium-lead amalgam.

Preparation of Materials

Two lots of lead amalgam were prepared, both containing 10% of lead. The first was prepared by electrolysis of a saturated lead chloride solution with a mercury cathode and a platinum anode. The lead chloride was prepared by adding redistilled hydrochloric acid solution to a solution of twice-recrystallized lead nitrate. The mercury was passed through a column of mercurous nitrate solution and redistilled at low pressure in a current of air.

The second lead amalgam was prepared by dissolving the required amount of lead in some of the above-described mercury. The lead was prepared by the method of Richards and Wadsworth⁸ from the twice-recrystallized nitrate.

The cadmium-lead amalgam was prepared by depositing cadmium by electrolysis in some of the first lead amalgam. By adding small amounts of the above-described mercury and lead, the composition was adjusted to 11% lead, 9% cadmium and 80% mercury, or 10, 15, and 75 atomic per cent., respectively. This composition is within the range in which the cadmium activity is constant.

The cadmium chloride and the cadmium iodide were both recrystallized twice.

The lead chloride and the lead iodide were prepared by precipitation from a solution of the twice-recrystallized nitrate, the first with redistilled hydrochloric acid solution and the second with a solution of recrystallized potassium iodide. Both were recrystallized.

Preparation of the Cells

The cells were set up in glass H-vessels of the type used for Weston cells.⁹ The amalgams were melted by heating, and cadmium-lead amalgam was placed in one leg of the vessel and lead amalgam was placed in the other. For the chloride cells some lead chloride was ground in a mortar with some cadmium chloride and was made into a paste with cadmium chloride solution. The paste was placed on top of the lead amalgam to a depth of at least 1 cm. Cadmium chloride crystals ground with some of the saturated solution were placed above the paste and also above the cadmium-lead amalgam. More crystals were then added, and the cells were filled to a point above the cross-arm with saturated cadmium chloride solution. The iodide cells were set up similarly. The

⁶ Kremann, Prammer and Helly, *Z. anorg. Chem.*, **127**, 306 (1923).

⁷ Vosburgh, *THIS JOURNAL*, **47**, 2531 (1925).

⁸ Richards and Wadsworth, *ibid.*, **38**, 223 (1916).

⁹ Vosburgh and Eppley, *ibid.*, **45**, 2269 (1923).

cells were usually evacuated to remove air bubbles, and the tops were flushed out with nitrogen and then sealed.

In the preparation of the first group of chloride cells, Cells 407-409, and the first group of iodide cells, Cells 340-342, the precautions previously described¹⁰ for the exclusion of oxygen in the preparation of Weston cells were taken. In the others no attempt was made to protect the materials from the air while the cells were being set up. In the case of the chloride cells this omission seemed to make no difference in the electromotive force, but it might have been the cause of the 0.2 mv. difference between the two groups of iodide cells.

In the first group of chloride cells the electrolyte contained a small amount of hydrochloric acid. The solution was made by saturating a 0.001 *M* hydrochloric acid solution with cadmium chloride. In the other cells the electrolyte was a saturated solution of cadmium chloride, or cadmium iodide, in redistilled water.

The first lead amalgam was used in all except Cells 456-459, in which the second lead amalgam was used.

Electromotive-Force Measurements

The electromotive forces were measured by means of a Leeds and Northrup thermocouple potentiometer. The potentiometer was accurate to 0.02% according to the data of the manufacturer. It was not checked. The standards were the Weston cells used as standards in previous investigations.¹¹ They were probably accurate to 0.01%. The standards were maintained in an oil thermostat at $25 \pm 0.02^\circ$ throughout the investigation. The experimental cells were kept in an oil thermostat capable of being maintained within 0.01° of the desired temperature. They were always maintained at constant temperature for a period of at least three days before important measurements. Tables I and II give the electromotive forces at 25° over a period of 8 and 9 months, respectively.

TABLE I

Cells	Cd(Pb, Hg) CdCl ₂ .2.5H ₂ O, SAT. CdCl ₂ .2.5H ₂ O + PbCl ₂ , SAT. Pb(Hg)				
	Electromotive force, 25°				
	1 month v.	2 v.	4 v.	6 v.	8 v.
407-409	0.13866	0.13869	0.13871	...	0.13807
429-430	.13870	.1386913822
456-45913873	0.13870	0.13865	...

TABLE II

Cells	Cd(Pb, Hg) CdI ₂ , SAT. CdI ₂ + PbI ₂ , SAT. Pb(Hg)				
	Electromotive force, 25°				
	1 month v.	3 v.	5 v.	7 v.	9 v.
340-342	0.10082	...	0.10088	0.10088	0.10082
427-428	.10065	0.1006510056	...

The chloride cells were quite reproducible. The average variation of the nine cells from the mean was about ± 0.03 mv., and the maximum variation was 0.13 mv. They were quite constant for a period of 4 to 6 months at least. The first two groups decreased somewhat in electromotive force after a change in temperature to 40° and back to 25° , as indicated by the values in the column of Table I headed 8 months. They

¹⁰ Vosburgh, *THIS JOURNAL*, 47, 1258 (1925).

¹¹ See Ref. 10, p. 1256.

became variable after this and one showed definite signs of deterioration.

The iodide cells were not as reproducible as the chloride cells. They did not give evidence of permanent change in electromotive force during the time they were under observation. The average variation from the mean of the 5 cells, when they were 1 month old, was ± 0.08 mv., and the maximum variation was 0.3 mv. The two groups differed by about 0.2 mv.

After constancy was assured at 25° , the temperature of the thermostat was changed successively to 20, 15, 20, 25, 30, 35, 40, 35, 30 and 25° , the cells being maintained at each temperature for 3 days to 2 weeks. The temperatures were measured by means of two platinum resistance thermometers and a mercury thermometer which had been checked by the Bureau of Standards. Temperatures were probably accurately measured to $\pm 0.01^\circ$.¹² Several electromotive-force measurements were made at each temperature. The chloride cells showed little hysteresis. After a temperature change, particularly after a decrease, the electromotive force usually changed a few hundredths of a millivolt over a period of 3 or 4 days. The iodide cells showed much more hysteresis. After an increase in temperature the electromotive force became too high. It decreased very slowly and never came to equilibrium in the time allowed before the next temperature change. With a decrease in temperature the effect was the opposite. The hysteresis was more pronounced in Cells 340-342 than in Cells 427-428.

The results of the measurements at different temperatures are given in Table III. Each value is the average of two measurements, one after an increase in temperature and the other after a decrease, except the values at 25° , 15° and 40° . At 25° the equilibrium value before the temperature was changed is given, and at 15° and 40° there was only one measurement at each temperature.

TABLE III
ELECTROMOTIVE FORCES AT DIFFERENT TEMPERATURES

Cells	Electromotive force					
	15° v.	20° v.	25° v.	30° v.	35° v.	40° v.
407-409	0.14030	0.13955	0.13872	0.13914	0.13997	0.14082
429-430	.14030	.13953	.13871	.13913	.13998	.14082
340-34209934	.10082	.10195	.10329	...
427-428	.09800	.09934	.10064	.10192	.10323	.10456

In the case of the iodide cells there was always a difference between the two values at the same temperature because of the hysteresis. In the case of Cells 340-342 this usually amounted to 0.3 mv. to 0.4 mv., but it was less than 0.1 mv. for Cells 427-428. It was obvious that neither of the two values represented the equilibrium condition, but it was assumed that the mean of the two would be approximately the equi-

¹² See Vosburgh, *J. Optical Soc. Am.*, 12, 513 (1926).

librium value. Calculated in this way the results for the two of iodide cells agreed very well.

Discussion

The Chloride Cell.—If the electromotive force of the cell



be plotted against temperature, the graph shown in Fig. 1 is obtained. The graph consists of two branches, one of which is a straight line, and the other, the one on the left, is nearly so. The two branches meet at about 26.2°. Below 26.2° the cell has a negative temperature coefficient,

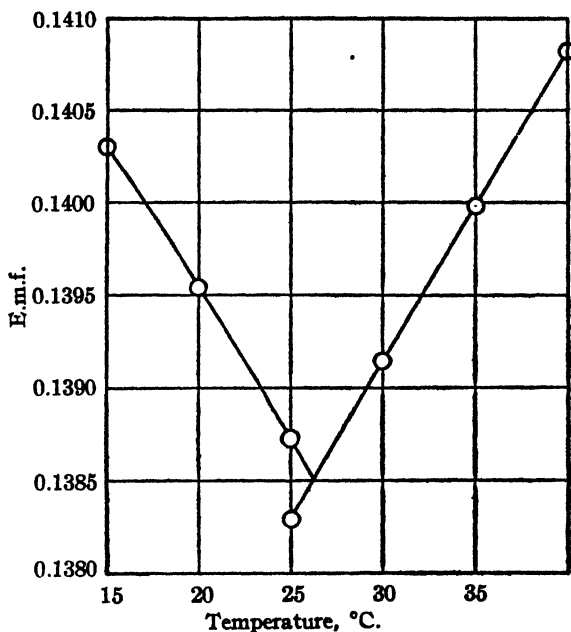


Fig. 1.—Relation between the electromotive force of the cell $\text{Cd(Pb, Hg)} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O, sat.} \mid \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} + \text{PbCl}_2, \text{ sat.} \mid \text{Pb(Hg)}$ and the temperature.

and above 26.2° it has a positive one. This is an indication of a transition point of some substance in the cell. According to Dietz¹³ and Cohen and Bruins¹⁴ the substance $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ is stable between -5 and 34° . Above 34° the monohydrate is the stable form. Fig. 1 gives no evidence of this transition point, the curve being a straight line between 26.2 and 40° .

Evidently as the temperature was raised from 25 to 30° transition took place. After the temperature had decreased from 30 to 25° , the

¹³ Dietz, *Z. anorg. Chem.*, 20, 257 (1899).

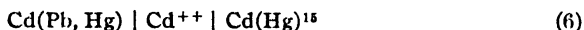
¹⁴ Cohen and Bruins, *Verslag Akad. Wetenschappen Amsterdam*, 25, 739 (1917).

last change in the series of measurements, the electromotive force at the latter temperature did not agree with the former values at 25°, but was abnormally low. It fell on the straight line representing the temperature-electromotive force relation above 26.2°, indicating that transition had not taken place when the temperature decreased from 30 to 25°. The electromotive force remained low for a considerable period and was somewhat erratic for several months after the temperature change. No abnormal behavior was noticed after any of the other temperature changes.

Between 15 and 26.4° the electromotive force of the chloride cell is given by the equation

$$E = 0.13872 - 0.000168 (t - 25) - 0.0000010 (t - 25)^2$$

This can be combined with the equation for the electromotive force of the cell



namely,

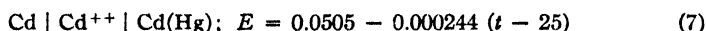
$$E = 0.00113 + 0.000025 (t - 25) + 0.0000002 (t - 25)^2$$

giving for Cell 1

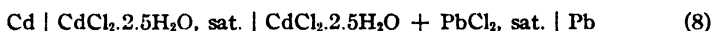
$$E = 0.13759 - 0.000193 (t - 25) - 0.0000012 (t - 25)^2$$

Obata found a value 3 mv. higher at 25°, while a value 5.6 mv. higher can be calculated from the results of Taylor and Perrott.

If the electromotive force of Cell 1 is combined with the electromotive force of Cell 4 and that of the cell¹⁶



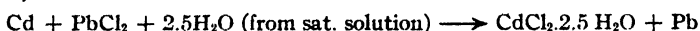
the electromotive force of the cell



is found to be

$$E = 0.1824 - 0.000453 (t - 25) - 0.0000012 (t - 25)^2$$

Therefore, for the reaction



$\Delta F_{25} = -8417$ cal., $\Delta S_{25} = -20.9$ and $\Delta H_{25} = -14,650$ cal.

Thermochemical data determined at temperatures of 18 to 20° are available for the calculation of the heat of reaction of this cell. Thomsen found $\Delta H_{18} = -93,240$ cal. for the heat of formation of cadmium chloride, and Braune and Koref¹⁷ found $\Delta H_{20} = -85,700$ cal. for the heat of formation of lead chloride. Cohen and Bruins¹⁸ found $\Delta H_{18} = -7110$ cal. for the heat change accompanying the formation of the hydrate of cadmium chloride in the saturated solution. Combining the thermochemical data, $\Delta H_{18} = -14,650$ cal., while from the data for Cell 8, $\Delta H_{18} = -14,420$ cal.

¹⁵ Ref. 7, p. 2534.

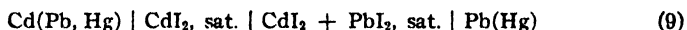
¹⁶ Gerke, *Chem. Reviews*, 1, 377 (1925).

¹⁷ Braune and Koref, *Z. anorg. Chem.*, 87, 183 (1914).

¹⁸ Cohen and Bruins, *Verslag Akad. Wetenschappen Amsterdam*, 26, 587 (1917).

The chloride cell would not make a good standard cell. Its temperature coefficient is large, and on account of the peculiar nature of the temperature-electromotive force relation, the discovery of another cell which could be combined with it to eliminate the temperature coefficient over a sufficient range of temperature is improbable. The formation of a metastable state after a decrease in temperature from 30 to 25° is a serious disadvantage. One of the cells failed toward the end of the temperature coefficient determination, and the others were in a metastable state and erratic after this determination was completed, making the constancy of the cells over long periods of time questionable.

The Iodide Cell.—The cell



has a practically linear temperature-electromotive force relation between 15 and 40°. It does not show any irregularity such as the chloride cell does. The temperature formula is not of the highest degree of accuracy on account of the hysteresis. The following should give the electromotive force within ± 0.1 mv.,

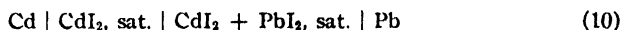
$$E = 0.1007 + 0.00026 (t - 25)$$

If the electromotive forces of Cells 6 and 9 are combined, the electromotive force of Cell 2 is found to be

$$E = 0.0996 + 0.000235 (t - 25) - 0.0000002 (t - 25)^2$$

This agrees within 0.1 mv. with the value found by Obata.

If the electromotive forces of Cells 2, 7 and 4 are combined, the electromotive force of the cell



is found to be

$$E = 0.1444 - 0.000025 (t - 25) + 0.0000002 (t - 25)^2$$

Therefore, for the reaction $\text{Cd} + \text{PbI}_2 \longrightarrow \text{CdI}_2 + \text{Pb}$, $\Delta F_{25} = -6664$ cal., $\Delta S_{25} = -1.15$ and $\Delta H_{25} = -7008$ cal.

The heat of reaction can be calculated from thermochemical data. Braune and Koref¹⁹ found $\Delta H_{20} = -41,850$ cal. for the heat of formation of lead iodide. Gerke²⁰ found a value in close agreement with this electrochemically. For the heat of formation of cadmium iodide, Thomsen found $\Delta H = -48,830$, while Taylor and Perrott²¹ found $\Delta H = -48,440$. The heat of reaction for Cell 10 on the basis of Thomsen's heat of formation is $\Delta H = -6980$ cal., and on the basis of Taylor and Perrott's heat of formation is $\Delta H = -6590$ cal. The agreement of the former with the value $\Delta H_{20} = -7034$ cal. calculated from the electromotive force and temperature coefficient of Cell 10 is very good.

¹⁹ Ref. 17, p. 180.

²⁰ Gerke, Ref. 4, p. 1703.

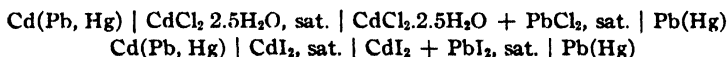
²¹ Ref. 2, p. 492.

The large and persistent hysteresis of Cell 10 and its large temperature coefficient are disadvantages to its use as a standard cell.

Other Cells.—A few cells were set up similar to Cells 5 and 9 but with bromide or sulfate electrolytes. Neither the cells with the bromide electrolyte nor those with the sulfate electrolyte were reproducible, and both groups of cells were variable. It is to be noted that Mellon and Henderson²² found that lead standard cells which contained a lead-amalgam-lead-sulfate electrode, were not constant when the electrolyte was a cadmium sulfate solution and were not as reproducible as the cells in which some other salts were used as the electrolyte.

Summary

The cells



were set up and their electromotive forces were measured over a period of several months at 25°, and also at 5° intervals from 15 to 40°.

The electromotive force of the first cell was not in agreement with the values of similar cells measured by Obata and by Taylor and Perrott. The electromotive force of the second cell agreed well with that of a similar cell measured by Obata.

The temperature-electromotive force relation of the cell with the chloride electrolyte indicated a transition point at a temperature between 26 and 27°.

Neither of these cells seems to be especially well adapted for use as a low-voltage standard cell, the chloride cell having a transition point which would interfere, while the iodide cell shows marked and persistent hysteresis. Both have large temperature coefficients.

The heats of reaction were calculated and compared with the heats of reaction calculated from thermochemical data.

NEWPORT, RHODE ISLAND

²² Mellon and Henderson, *THIS JOURNAL*, **42**, 680 (1920).

AN EXPERIMENTAL TEST OF THE GIBBS ADSORPTION THEOREM: A STUDY OF THE STRUCTURE OF THE SURFACE OF ORDINARY SOLUTIONS¹

BY JAMES W. MCBAIN AND GEORGE P. DAVIES

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The object of this communication is to present a definite conception of the structure of the surface of ordinary solutions as deduced from several different kinds of evidence and confirmed rather directly by absolute measurements of adsorption in and near the surface of solutions.

A clear picture of the structure of films of insoluble materials resting upon a solvent such as water has been gained through Rayleigh, Hardy and Adam in England, Devaux and Bancelin in France and Langmuir and Harkins in America. For example, a film of the insoluble palmitic acid on water is a coherent monomolecular film, all the molecules being oriented perpendicular to the surface. Far less has been known about soluble materials and about the two fundamental questions as to whether in such cases monomolecular films are formed and as to how far beneath the surface the influence of surface forces such as adsorption and orientation extends.

Some of the conceptions resulting from the adsorption of a soluble substance in the surface of a solution are illustrated in Fig. 1. Langmuir, in 1917, suggested that the adsorbed layer of dissolved substance might well appear as a monomolecular layer upon the surface (Fig. 1a). The data which he obtained from calculation in the absence of any direct measurements corresponded, however, to a curiously incomplete, although constant, monomolecular layer (Fig. 1b). To explain this discrepancy Donnan, in 1923,² suggested that the molecules were partially submerged and, therefore, separated in the surface (Fig. 1c), whereas Langmuir suggested hydration of each molecule or alternatively that in some cases such as phenol and aniline the molecules lie flat instead of standing in their usual orientation.

The present communication affords for the first time accurate measurements of the absolute amount of adsorption and in each case the amount actually adsorbed is definitely greater than that which could be packed on the surface as a monomolecular film. Hence we suggest that there is probably a fairly complete monomolecular film upon the surface, but that in addition to this there is an excess concentration, or adsorption, within the solution in the immediate neighborhood of the surface, ex-

¹ Read before the Mid-West Regional Meeting of the American Chemical Society at Madison, Wisconsin, May 28, 1926.

² Presidential address, Section B, British Association for the Advancement of Science, 1923; *Nature*, 112, 869 (1923).

tending inwards for many molecular diameters (Fig. 1d). This is shown in Fig. 1d as consisting of chains of oriented molecules extending inwards from the surface into the solution.

Previous Evidence that a Surface Layer Has Depth.—

(1) The classical experiments of Hardy on lubrication have shown that a liquid between two metal surfaces can exhibit static friction even when the liquid layer is far deeper than the diameter of a molecule. This appears to be the first clear evidence that orientation of molecules may extend far below the actual surface. Of the two possible explanations of this undoubted effect, namely, either that the range of molecular attraction is great as compared with molecular diameter or, alternatively, that it is through a sort of chain effect that molecules are successively oriented through the depth of the liquid, of these we would prefer the second, although Hardy has favored the first.

(2) The studies of adhesion by McBain, Hopkins and Lee³ have shown that a thin film of adhesive between two surfaces may yield a joint several times as strong as the adhesive substance itself. Furthermore, the thinner the layer of adhesive the stronger the joint, and this influence becomes especially great when the films are excessively thin. These results we would likewise interpret in terms of the chain effect of orientation of molecules in the neighborhood of the surface.

(3) Other evidence is provided by the study of the viscosity of liquids

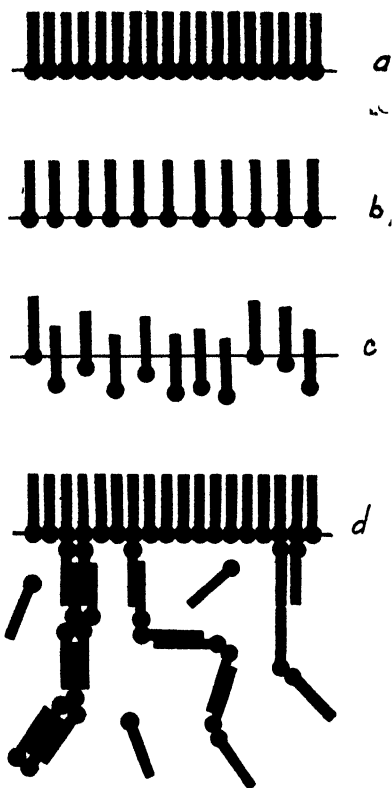


Fig. 1.—Diagrammatic representation of various conceptions of the structure of surfaces of ordinary solutions; (a) close-packed monomolecular layer of solute upon the surface, (b) curious incomplete monomolecular layer obtained by calculation using the simplified Gibbs' concentration adsorption formula, (c) Donnan's attempted explanation of (b) by assuming partial submergence, (d) the conception advanced in the present paper, a complete monomolecular film plus chains of oriented molecules of solute extending far below the surface.

³ (a) McBain and Hopkins, *J. Phys. Chem.*, 29, 188–204 (1925); (b) Second Report of the Adhesive Research Committee, Appendix IV, 34–89 (1926); (c) *J. Phys. Chem.*, 30, 114–25 (1926); (d) McBain and Lee, *Proc. Roy. Soc. (London)* 113A, 605–20 (1927); (e) *J. Soc. Chem. Ind.*, 46 (1926); (f) *Ind. Eng. Chem.*, 19, 1005 (1927).

in which solid particles are suspended. Hatschek⁴ has proved that even in the simplest of such systems the viscosity coefficient alters with the rate of shear, a phenomenon for which he has been at a loss to account. It cannot be due to solvation or aggregation of particles in such a system as starch granules suspended in the indifferent liquid, toluene; but it is in obvious agreement with the conception that a chain effect extends into the liquid from any solid surface which has oriented any of the superficial molecules. Tests should be carried out with polar liquids where this effect would be expected to be greatest; likewise with solutions such as aqueous *p*-toluidine.

(4) The most direct method of studying the structure of surfaces is by measurement of the absolute amount of adsorption in and near the surface. Euler⁵ has attempted absolute measurements of adsorption on gold and silver foils from solutions of silver nitrate, obtaining a result which is about double that for a monomolecular film of silver ions for this area of surface, assuming that the silver surface was smooth and continuous. This accords with our interpretation as illustrated in Fig. 1d, that is, a monomolecular layer in addition to the adsorption or excess concentration in the neighborhood of the solid surface. It should be borne in mind that adsorption in the surface of a liquid medium is very different from adsorption from a vapor or gas, because whereas in the liquid or solution the space below the surface is closely packed with contiguous molecules which merely have to be oriented, in the latter case the only molecules appreciably near the surface are those which are actually captured or adsorbed by the surface, and hence the surface effect cannot reach out from the actual surface into the gaseous space.

(5) In earlier experiments by W. C. M. Lewis⁶ to determine the adsorption of various materials at a liquid-liquid interface, in nearly every case the approximate adsorption as determined was mostly much larger than expected, often 100 times larger. However, many of these substances were colloidal and the results are ambiguous.

(6) The only determinations of the absolute adsorption of a substance from true solution at the air interface are those of Donnan and Barker,⁷ sixteen years ago, who employed an aqueous solution of nonylic acid. They blew a stream of air bubbles up through the solution which was placed in a simple still-head divided into a number of compartments

⁴ (a) Hatschek, *Proc. Phys. Soc. London*, **28**, 274 (1916); (b) *Kolloid Z.*, **40**, 53 (1926); (c) *J. Phys. Chem.*, **31**, 383-392 (1927); (d) Friday Evening Discourse, Royal Institution, March 18, 1927.

⁵ (a) Euler, *Arkiv. Chem., Mineral. Geol.*, **7**, No. 31, 16 pp. (1920); (b) *Z. Elektrochem.*, **28**, 2-6 (1922).

⁶ (a) Lewis, *Phil. Mag.*, **15**, 499 (1908); (b) **17**, 466 (1909); (c) *Z. phys. Chem.*, **73**, 129 (1910).

⁷ Donnan and Barker, *Proc. Roy. Soc. (London)*, **85A**, 557 (1911).

vertically above each other. They considered (erroneously, see below) that the partitions would prevent mixing of the liquids in the several compartments. They took for analysis the whole of the liquid except that in the uppermost compartment and, after mixing it until homogeneous, determined the loss of nonylic acid. They do not record any measurement of a corresponding gain in the uppermost compartment, neither was there any test of the effect of altering the age of the bubble or time of contact between air and solution. From the number and dimensions of the bubbles which had passed through the solution they knew the total area involved and they estimated the surface tension by means of drop numbers, using this also as their means of analysis. They compared their results with those computed from the surface-tension curve by means of the so-called Gibbs theorem: Γ , the excess of nonylic acid in the interface = $-\frac{c}{RT} \cdot \frac{d\sigma}{dc}$, where c is the concentration and σ the surface tension. Some uncertainty attached to the degree of dissociation in these extremely dilute solutions; in the results collected in Table I, four calculated values are given for comparison with Donnan and Barker's observations taken from Donnan and Barker's curve and Forch's curve for surface tension, respectively, calculated in each case for " i " alternately equal to 1 or equal to 2, that is, for no dissociation and for complete dissociation of nonylic acid.

TABLE I

THE OBSERVATIONS OF DONNAN AND BARKER ON THE ADSORPTION, Γ , OF NONYLIC ACID IN THE AIR-WATER INTERFACE COMPARED WITH THE VALUES PREDICTED FROM THE SO-CALLED GIBBS THEOREM

Concn. of soln., %	Γ obs., g. $\times 10^{-8}$	- Γ calcd. (g. $\times 10^{-8}$)—			
		Forch's curve " i " = 1	" i " = 2	Donnan's curve " i " = 1	" i " = 2
0.00243	9.5	5.8	2.9	5.5	2.6
.00500	15.2	12.3	6.1	11.4	5.7
.00759	10.9	15.8	7.9	12.6	6.3
.00806	9.15	16.3	8.1

* " i " is the degree of dissociation of nonylic acid in these solutions.

Since these four numbers constitute the only careful test of the adsorption in the air-water interface hitherto published, it is necessary to scrutinize them closely. They can be considered as confirming the order of magnitude of the effect but they are subject to serious error, as will be shown. Since they must be regarded as only semi-quantitative, no stress need be laid on the fact that they do not conform to Langmuir's prediction that they should reach a constant maximum value with increase of concentration; neither need attention be paid to the fact that the result of 10×10^{-8} g./sq. cm. gives an area of 26×10^{-16} sq. cm. per molecule, which is distinctly less than monomolecular and corresponds to the state of

affairs that is illustrated in Figs. 1b or 1c. Our reason for regarding the method as inherently erroneous is given in the following paragraph describing extensive series of careful determinations (about 100) carried out during several years in the Bristol Laboratory, and all discarded.

Rejection of All Results by the Donnan and Barker Method.—There is a close resemblance between the determination of transport numbers and a determination of adsorption by the stream of bubbles used in the Donnan and Barker method. In the first the transport is electrical, in the second the bodily movement is mechanical. In the first, a careful experiment requires a demonstration that the gain or loss in the anode compartment is equal to the loss or gain in the cathode compartment and that the middle portion is unchanged. In precision work it is customary to take a series of middle portions to avoid chance compensation. We had taken all these precautions, analyzing every portion separately by the accurate method of the Zeiss interferometer and testing the effects of concentration, time, total area, etc.

There is one fatal objection to all measurements by this method, that is, the pumping action that goes on throughout the apparatus every time a bubble is injected and passes through. Donnan and Barker were misled by a strange blank experiment in which they observed no mixing. Within each compartment the stream of bubbles necessarily causes rapid stirring, so that the liquid in each compartment is kept sensibly homogeneous. As each bubble is passed into the bottom of the apparatus its own volume of liquid is necessarily pumped into the next compartment above, and a similar volume of liquid is returned when the bubble leaves each of the compartments successively. Since there are perhaps 24,000 separate bubbles it is easy to compute the amount of mixing that is inevitable, given the size of bubble relative to a given compartment. Hence a stationary state is reached which is definitely illusory, giving much less than the true adsorption.

THE STOPPER METHOD.—We tried a method of circumventing the mixing between successive compartments by carefully arranging the diameter and rate of passage of the bubbles and the dimensions and form of the orifices between compartments so that no bubble should leave an orifice until the next bubble had just caught up to it and taken its place. With care a third bubble could be added so that two at a time acted as stoppers in each orifice. Great care is necessary to prevent the bubbles from actually touching the glass, through breakdown of the thin film of liquid between, and also the dimensions of orifices of the successive compartments have to be adjusted to the lessening hydrostatic pressure as the bubbles travel upwards. Hence this difficult technique was discarded in favor of the very easy experiments to be described later.

The Nature of the Findings of the Present Investigation.—The meas-

measurements to be described for solutions of *p*-toluidine, of camphor and of amyl alcohol give quantitative information as to the amount of adsorption per square centimeter of surface of their aqueous solutions. In the first place, the amount of adsorption which occurs is definitely much greater than the material which could be packed into a monomolecular layer according to the dimensions of molecules obtained from the study of insoluble films and from x-ray measurement of crystals. For example, there is one molecule of toluidine adsorbed for every 14×10^{-16} square centimeters of surface, whereas one molecule can cover 23×10^{-16} square centimeters of surface. One molecule of amyl alcohol is absorbed for each 9×10^{-16} square centimeters of surface, whereas it should cover 21×10^{-16} square centimeters. These and the similar results for camphor show that the measured adsorption is several times greater than the amount of material which can be accommodated in a monomolecular layer and we, therefore, deduce an arrangement such as that depicted in Fig. 1d, where adsorption occurs not only upon the surface but within it. This shows that surface forces and surface tension are conditioned not solely by the outermost layer of molecules but also by much deeper layers. The study of the surface tension of ordinary liquids by such investigators as Sugden⁸ has pointed to the similar conclusion that the total surface energy of a liquid is not defined entirely by the nature and orientation of the surface layer of molecules. Fig. 1d goes further in that it suggests a mechanism for this effect.

A second important result following from our numerical data is that the so-called Gibbs theorem, in which adsorption is related to concentration and surface tension, is shown to give highly erroneous values differing by several fold from those actually observed. Hence, this commonly used concentration formula must be rejected as being of only qualitative significance. In the following pages our method of experiment and its numerical results will be presented and afterwards it will be shown that a more careful consideration of the requirements of the true Gibbs formula, which involves thermodynamic quantities and all the components of the system (such as the gas used in bubbling) is required for adequate treatment on this subject.

Other Relations That Follow from the Conception of Chains of Oriented Molecules Extending Inwards from the Surface.—If this conception is correct it should find manifold applications and one should seek information in very diverse fields. For example, it affords an explanation of the otherwise surprising effect of inert fillers upon the strength and resiliency of rubber, as in rubber tires. It explains why extremely fine subdivision produces the greatest effect; the whole of the very extensive surface has the role of orienting the molecules in immediate contact with it and the

⁸ Sugden, *Trans. Faraday Soc.*, 22, 486 (1926).

chain effect extends with diminishing intensity into the surrounding rubber. Fine subdivision not only increases the surface but diminishes the distance between these orienting particles.

In a similar fashion inert fillers should increase the strength and elasticity of layers of adhesives, thus improving joint strength where the layers are not excessively thin (see Second Report of the Adhesives Research Committee, Appendix IV, 109-111 (1926)). Perhaps we have here the explanation of the effect of multiple gluing in increasing the strength of a joint, that is, the well-known great increase in strength of many joints when the adhesive is applied in successive thin coatings and each allowed to dry before the next is applied, and a final coat given just before the surfaces are brought together. Probably we fix successive chains before applying the next layer. All these suggestions should be accessible to direct experimental test.

Even the effect of oil upon troubled water, which Hardy has had to ascribe to the diminishing of its friction against the atmosphere may possibly be brought under this explanation, since the oil forms a stable film to which chains of stable molecules may be anchored. In other words, the conception assumes that a liquid is not always a liquid near its own surface but may become a semi-solid.

Even a pure liquid has been shown by H. B. Baker and others to consist of a mixture of simple and aggregated molecules and hence the composition and structure of the surface will be different from that of the bulk of the liquid. Several writers such as L. V. King and Ramden have shown that from physical and especially optical considerations, there is a tendency towards formation of minute protocrystalline aggregates of molecules throughout liquids, and this tendency must be greatly enhanced and given direction in the neighborhood of surfaces.

A New and Simple Method of Determining Absolute Adsorption in the Air-Water Interface

There are many possible ways of replacing the discarded Donnan and Barker method. The following is one of the simplest. It gives quantitative results accurate to a few per cent. and only a few hours are required for each determination. The principle is to use a long inclined tube of large diameter (1.6 meters long), so inclined that bubbles pass slowly along it, adsorbing to saturation value without appreciably altering the concentration of the liquid remaining in the tube, which thus acts as a reservoir. At the top of the incline the bubbles rise into a vertical tube so narrow that each bubble fills its diameter. Each bubble in the vertical tube rapidly overtakes the former ones and draining is so rapid that within a few inches there is a continuous column of cylindrical bubbles in contact with each other. At the height at which draining is found to be sufficiently complete the narrow tube is curved over and down. The films break in the downward portion of the tube, condensing to a liquid, which is caught and analyzed for comparison with the original solution. By changing the degree of inclination of the long, sloping reservoir the bubbles can be kept in contact with the solution for any desired period of time; but in the vertical tube the bubbles must not be allowed to burst

before they have gone round the bend. In the case of the very unstable bubbles from aqueous *p*-toluidine the four seconds during which these films last is ample for this purpose. To forestall a possible source of criticism (see later) the films should be allowed to break within the narrow tube before they reach its exit.

The apparatus is shown in Fig. 2. Nitrogen from a cylinder fitted with a constant pressure regulator is purified by passing through aqueous sodium hydroxide and is then

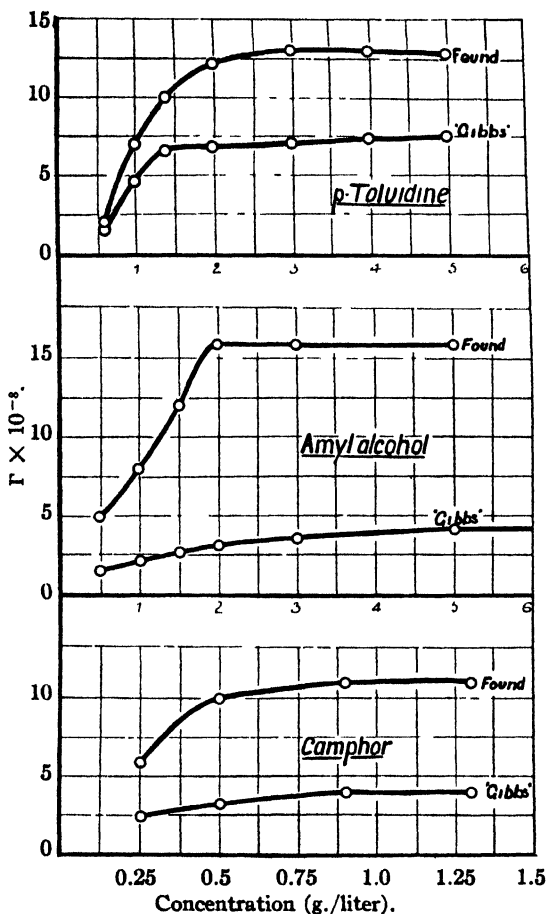


Fig. 2.—Comparison of absolute adsorption measured by the authors with that calculated from the so-called "Gibbs" (concentration) formula.

saturated with the vapors of the solution which is to be measured, first by bubbling it through a sample of that solution and then by passing it through a Washburn saturator filled with another sample of the same solution for final adjustment. The pressure is steadied by a capillary tube after which the gas bubbles into the apparatus through a suitably designed jet. The bubbles slowly pass up the long, inclined tube and rapidly up the narrower vertical tube, each pushing the previous ones out of the top of the liquid toward the vessel where the liquid from the collapsed films collects. From here the

nitrogen, still saturated with the vapors from the solution, passes through a Parkinson and Gowan flow meter, previously calibrated by passing through it a known volume of air from a large gas holder. It was found that the volumes recorded by this instrument differed from the true values by less than one per cent.

It is essential that the narrow vertical tube be kept thoroughly wet so that bubbles do not break or come into real contact with the glass. For this purpose a further supply of original solution is provided in the supplementary reservoir and this is allowed to flow slowly into the apparatus until the orderly arrangement of bubbles and films has been fully attained. Thereafter, only such solution is supplied as is required to maintain the level of the liquid in the vertical tube constant at the optimum height. The experiment begins when this steady state has been set up; a fresh collecting vessel is put on and the first reading on the flow meter taken. When sufficient nitrogen is passed, that is, when a sufficient volume of liquid from collapsed film has been collected, the bubbling is stopped, the time taken, the flow meter read and disconnected and the collecting vessel stoppered and weighed. About 30 cc. of the solution is allowed to flow out through the narrow tube and collected in a separate vessel. The solution remaining in the inclined tube is all collected in the top reservoir, by applying gentle suction, and well mixed. The three solutions are then each analyzed in duplicate, using a Zeiss refractometer which determines the refractive index to about one division, which corresponds in the case of *p*-toluidine to about 1.49×10^{-6} g. of toluidine per cc. of solution. This is probably the most accurate method of analysis for such binary liquids.

Blank experiments were performed which showed that the method of cleaning and filling the apparatus was efficient, for the samples taken as in an experiment, but without any bubbling, were identical with the original solution. An essential blank experiment is one to show that saturation of the nitrogen is accurate, so that the nitrogen which escapes from the flow meter should neither impoverish nor enrich the solution under investigation as it passes through. For this purpose it was only necessary to allow the gas to pass through as usual but with the level of the liquid in the vertical tube sufficiently lowered so that no films escaped. Under these conditions we found that the concentration of the solution was completely unaffected by the passage of the previously saturated nitrogen. This is of great importance in the final considerations of the results which cannot be ascribed to this possible source of error.

If a thin surface film of toluidine solution of volume v and exposed area s be removed from the reservoir of liquid of original concentration c_0 to the collecting vessel, and if the actual surface contains its equilibrium amount of adsorbed toluidine Γ , then the weight of toluidine in the collecting vessel will be equal to $c_0v + \Gamma s$, and for n such films $c_0nv + \Gamma ns$. The volume of the solution in the collecting vessel V would be nv and its concentration c_1 will be $c_0 + \Gamma ns/v$; whence $\Gamma = [(c_1 - c_0)V]/ns$. In deriving this equation it is assumed that c_0 , the concentration of the solution from which the films were taken, remains unchanged during the removal of the film, whereas in practice a relatively small but finite decrease will occur. If the final concentration of the remaining solution is c_f , then since $c_0 - c_f$ is very small compared with $c_1 - c_0$, then the in-

crease in the concentration c_1 of the solution collected over that in the reservoir will be $c_1 - (c_0 + c_f)/2$ instead of $c_1 - c_0$. Hence $\Gamma = (V/ns) \cdot [c_1 - (c_0 + c_f)/2]$. The detail of the experimental procedure is best illustrated by giving the data of an actual experiment in full.

Experiment 4 of Section V.—Twenty-four minutes were required for this experiment during which the flow meter registered the passage of 0.05 cu. ft. = 1420 cc. The rate of formation of films (or bubbles) was 100 in 74 seconds at the beginning, at the end and throughout the experiment. The time of contact between bubble and solution in the reservoir was 14 seconds, many previous experiments having shown that no further adsorption occurred after 4 seconds, hence a threefold margin of time is always allowed.

The volume of solution collected from collapsed films (weighed) was 38 cc. A further sample of 38 cc. of liquid was allowed to flow out through the vertical tube and 350 cc. remained in the reservoir. The original solution contained 1.000 g. of toluidine per liter and when placed in a 4cm. cell in the interferometer and compared with water produced a change in reading of 640 divisions on the micrometer screw (this deflection being directly proportional to the difference in concentration, one division corresponding to 1.49×10^{-6} g. per cc.). The liquid collected from the collapsed films showed a gain over the original solution of 20 divisions, the sample of liquid taken from the vertical tube likewise showed a gain, although of only one division, showing that the transport of toluidine by the films is not quite complete. This increase was added to the other liquid collected. The final solution in the reservoir showed a loss of between 3 and 4 divisions. Hence, the total change in total concentration of the solutions collected relative to the mean concentration of the initial and final solution in the reservoir is 23 divisions. Hence, the total transport of toluidine = $V[c_1 - (c_0 + c_f)/2] = 38 \times 23 \times 1.49 \times 10^{-6} = 1.3 \times 10^{-3}$ g. The total number of bubbles, n , = 1950. Hence the volume of each bubble is 1420/1950 cc. Each bubble in its final form is a right cylinder of radius 0.65 and, therefore, of length 0.55 centimeters. The total area of these cylindrical bubbles is equal to $1950 \times 2\pi \times 0.65 \times 1.2 = 9550$ square centimeters. Hence $\Gamma = \text{total transport}/ns = 13.6 \times 10^{-8}$ g.

In this particular experiment there was a slight decrease in concentration in the residual solution due to evaporation and loss of toluidine. The total gain in the liquid from the collapsed films is, therefore, rather less than observed in the original solution. In better experiments the two were equal within the experimental error. This is very important because, as has been mentioned, the gain in toluidine is twice as great as that corresponding to a monomolecular film or to that calculated from the so-called Gibbs concentration formula.

The partial pressure of *p*-toluidine above its aqueous solution has been

measured in the Bristol Laboratory by F. H. Pollard. From his results one may deduce that the partial pressure of *p*-toluidine of the solution used above was about 0.0078 mm. at 16°. The total volume of nitrogen passed through, namely, 1420 cc., exactly saturated with this vapor would, therefore, contain 6.6×10^{-5} g. of toluidine. Now the total amount of *p*-toluidine adsorbed and transported in the surface was 129.9×10^{-5} g. Hence, since the total amount of toluidine in the gaseous phase is only a few per cent. of the amount actually transported in the surface of the bubbles, any lack of adjustment in the saturation of the nitrogen with the vapors of the solution must leave the final experimental result of $\Gamma = 13.6 \times 10^{-8}$ g. per sq. cm. almost unaltered.

The Effect of Size of Bubble upon the Value Obtained.—If it is the true value of the adsorption Γ that is obtained by these measurements, they should be independent of the actual surface used. The following series of experiments shows the effect of keeping all other conditions constant and varying only the size of bubbles in the same tube. This appears as a variation in the length of the cylindrical bubbles or in the distance apart of the visible films when the bubbles have drained after coming into contact. The results are collected in Table II.

TABLE II
THE EFFECT OF VARYING THE LENGTH OF BUBBLE UPON THE APPARENT VALUE OF THE ADSORPTION*

Length of cylinder, cm.	Total surface area (sq. cm.)	Γ in g./sq. cm., obs.
5.5	43,000	4.5×10^{-8}
2.5	25,000	8.4×10^{-8}
1.5	19,300	12.7×10^{-8}
1.2	23,000	13.0×10^{-8}
1.1	24,000	14.5×10^{-8}
0.75	17,200	14.8×10^{-8}
.57	12,500	14.7×10^{-8}
.52	15,300	14.9×10^{-8}
.36	13,600	14.5×10^{-8}

* Solution 4 g. toluidine per liter. Internal diameter of the vertical tube 1.30 cm.

The results in Table II, properly interpreted, show the validity of this method of measuring Γ and likewise reveal under what conditions true values are obtained. It is seen that as soon as the cylindrical bubbles are appreciably shorter than their diameter the value of Γ observed is constant and independent of further alteration in the surface area. This is readily understood when we consider the propulsive and retarding forces which act upon a cylindrical bubble passing up a tube. If the bubble is short it will move as a whole. If the bubble is very long in comparison with its diameter the propulsive force is applied to its ends, whereas frictional retarding force is applied to its sides, and if the bubble is long enough the middle part of the cylindrical sides will not move, even al-

though separated from the glass walls by a finite thickness of aqueous solution. In the extreme case there will be a succession of flat films representing the ends of the bubbles pressing up through a tube lined with a film of the same or slightly greater concentration. Hence, in such a case the method cannot be expected to give correct results since the surface taken for the calculation is the whole internal area of the bubble whereas only the ends are actually transporting toluidine. As a check upon this it can be seen that the values for Γ in the last column of Table II become almost constant if it is assumed that only 1.1 cm. of the length of each bubble can actually be moved. Of course there will always be a residual drag which will be reflected in a slightly greater transport if the liquid remaining in the vertical tube is collected and analyzed. In the experiment quoted above this represented 1 division out of 23 expressed in interferometer readings. The length of the bubble usually employed throughout the final measurements was about 0.5 cm. and never exceeded 1 cm. In every experiment it was found that the value for total transport, as calculated from the decrease in concentration of original solution was, within the limits of analytical error, equal to that obtained from the increased concentration of the solution produced from the collapsed films. This is important as proving that the final movements of the bubbles did not extract toluidine from the previously saturated stream of nitrogen passing through. This proves, too, that even though there must be a drag upon any bubble passing through any solution, and hence a tendency towards thinning out or renewal of the forward surface and a corresponding thickening or concentration at the rear surface, the error introduced in the particular substance we have investigated can be only very slight. It might be far otherwise with any substance whose adsorption is quick and desorption slow but if such a substance were volatile, as ours are, the effect would be at once detectable by impoverishment of the gaseous phase which we have shown not to occur in our experiments. This argument is vital to the acceptance of our numerical values. It so happens that the partial pressure of the toluidine above the solutions is such that there is just about as much toluidine in the gaseous phase within each bubble as is adsorbed upon the surface of the bubble. Hence, if the nitrogen were robbed of all its toluidine the observed transport would be doubled, but since this effect did not occur this source of error is measurably absent. In other words, our results can only be a few per cent. too great. For the reason stated no dynamic method can be perfect and the ideal method must be static.

Experimental Results for the Adsorption of *p*-Toluidine in the Nitrogen-Water Interface

Our numerical data are collected in Table III, which gives the results for solutions of *p*-toluidine ranging from 0.6 g. per liter up to saturation.

TABLE III

ABSOLUTE MEASUREMENTS OF THE ADSORPTION OF *p*-TOLUIDINE IN THE SURFACE OF ITS AQUEOUS SOLUTION

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (diva.) uncorr. corr.		Cc. of film soln.	$\Gamma \times 10^3$ obs. g./sq. cm.
0.6	0.62	8100	3	3		2.3
	.67	10000	4	4		2.3
	.66	10500	5	5		3.0
	.71	11700	3	3		2.0
	.73	13000	5	5		2.5
	.69	12000	4	4		2.1
					Mean =	2.4
1.0	0.55	7700	7	7	45	6.1
	.68	10200	9	10	45	6.6
	.79	9600	8	8	47	5.9
	.66	10500	9	10	44	6.3
	.70	7600	7	8	46	7.2
	.96	6600	7	8	42	7.6
					Mean =	6.5
1.40	0.60	9200	13	14	45	10.2
	.70	11000	15	17	53	12.1
	.55	7620	10	12	45	10.5
	.59	9200	13	14	45	10.2
	.59	9230	12	13	44	9.4
	.57	7500	11	12	42	10.0
					Mean =	10.4
2.0	0.62	10900	16	18	51	13.3
	.53	9800	14	16	52	12.7
	.58	11000	19	21	42	11.9
	.58	11200	19	21	46	12.9
	.63	8900	13	16	50	13.4
	.62	6250	11	12	42	12.1
					Mean =	12.7
3.0	0.61	10800	24	27	38	14.1
	.54	9600	15	18	47	12.9
	.67	10400	17	20	50	14.3
	.56	9500	20	23	38	13.6
	.60	10900	21	24	41	13.5
	.58	11200	21	23	40	12.4
	.56	7600	11	14	47	12.9
					Mean =	13.4
4.0	0.51	12000	30	33	34	13.9
	.49	10140	30	34	26	13.0
	.50	12130	24	27	42	13.9
	.49	13230	28	32	37	13.3
	.56	11300	28	32	32.5	13.7
	.53	11750	26	29	33	12.2
	.52	11860	26	30	33	12.4
					Mean =	13.2

TABLE III (Concluded)

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film soln.	$\Gamma \times 10^3$ obs. g./sq. cm.
			uncorr.	corr.		
5.0	0.47	12500	31	34	31	12.0
	.54	11560	29	30	33	12.8
	.48	13300	28	29	34	11.3
	.53	12660	27	31	38	13.8
	.50	11500	23	32	34.5	14.2
	.48	12280	26	30	38.5	14.0
					Mean =	13.0
6.0(satd.)	0.41	11700	20	23	30.5	9
	.54	15300	25	27	33.5	8.5
	.43	10500	21	24	28.5	9.5
					Mean =	(9)

The two extreme concentrations yield only approximate results because in the most dilute solution the absolute change is small and in the saturated solution the liquid from the collapsed films was supersaturated and before analyses could be carried out a few small crystals of toluidine were observed to separate. Thus the true value must be greater than that actually recorded. Sufficient data are given to show the degree of reproducibility of the experiments and to estimate the approximate error in the results. The toluidine was obtained from Kahlbaum and well recrystallized, m. p. 45.6°. The solubility measured by Edwards was 0.654 g. in 100 cc. of water at 15°. Conductivity water was used as solvent. The temperature was 16°.

Comparison of the Adsorption Observed with the Amount Needed for a Monomolecular Film

It is of course impossible to measure directly the amount of a soluble substance which is required to form a true monomolecular film. There are, however, two other means of estimating the dimensions of the molecule. The first is by comparison with substances higher in the homologous series which are sufficiently insoluble and whose area has been directly measurable by the film method. For example, Adams has found the area covered by a single molecule of hexadecylaniline in a close-packed monomolecular film on water to be 24×10^{-16} sq. cm. and for hexadecylphenol 24×10^{-16} sq. cm., whereas we have found one molecule of toluidine for each 14×10^{-16} sq. cm. of available surface. Even if shorter molecules might be packed slightly more closely than longer ones and even if through competition there were a tendency for the monomolecular film of a soluble material to be rather more closely packed than an insoluble film, the discrepancy is undoubted and clearly points to the conclusion that there is not room on the surface for all of the adsorbed material.

The extent to which molecules in a monomolecular film can be compressed is limited by the dimensions of the molecules themselves and these

are given by x-ray analysis of the solid crystals. The toluidine molecules occupy the minimum area when oriented perpendicular to the surface. The dimensions of molecules containing the benzene ring have been obtained by Bragg using naphthalene⁹ and by Shearer using benzene.¹⁰ From the data for naphthalene it has been concluded that the area of cross section of a benzene ring is 25×10^{-16} sq. cm., while Shearer obtained from the unit cell of benzene itself a cross-sectional area of 23.3×10^{-16} sq. cm. Both of these agree with the dimensions of a single molecule in a monomolecular film but show that if there is one molecule of toluidine for each 14×10^{-16} sq. cm. not much more than half can be upon the actual surface.

The Change of Surface Tension with Concentration

Our measurements have demonstrated that the adsorption is constant over a wide range of concentration and that nevertheless the surface tension continues to fall with increase of concentration even after this constant value has been attained. This requires explanation. At first sight it might have been expected that the surface tension should be constant once the monomolecular film on the surface had been formed and the adsorption was constant. The surface tension as measured experimentally may be regarded as being the sum of the surface tension of the exposed outer surface of the monomolecular film of *p*-toluidine plus the interfacial tension between the film and the solution. This is the expression used by Antonoff¹¹ for the surface tension of a complete film and verified by him for the benzene in water system. The surface tension of the film is taken as constant since the molecules therein have a constant orientation and resemble those in the surface of liquid toluidine in bulk. Hence in applying this conception to the present systems, namely, unsaturated solutions, which are more complicated than the saturated systems hitherto studied, it is necessary to ascribe any change in total surface tensions to change in the interfacial tension between the monomolecular film and the solution upon which it rests.

Morgan and Egloff¹² studied the partially miscible liquids phenol-water and found at saturation the surface tension of each of the two layers was the same as the surface tension of pure phenol. For regions in which only one layer could exist they found that the addition of phenol lowered the surface tension until at saturation it was that of pure phenol. Similar behavior was found with solutions of amyl alcohol and triethylamine. We, therefore, conclude that in our system, aqueous toluidine,

⁹ Bragg, *Proc. Roy. Soc. (London)*, **35**, 167 (1923).

¹⁰ Shearer, *Proc. Phys. Soc. London*, **35**, 81 (1922).

¹¹ Antonoff, *J. chim. phys.*, **5**, 392 (1907). See also Iredale, *Phil. Mag.*, **49**, 466 (1921), who verified this expression for a monomolecular film of water on mercury.

¹² Morgan and Egloff, *THIS JOURNAL*, **38**, 844 (1916).

the saturated solution should have approximately the same surface tension as liquid toluidine, that is, the surface tension of the outside layer of *p*-toluidine molecules. This assumes that in this saturated solution there is no interfacial tension between the film and the aqueous layer. The suggestion thus derived may be summed up in the statement that the more concentrated the solution, the less disparity will exist between it and the monomolecular film on its surface, and the less, therefore, will be its interfacial tension. The interfacial tension will, therefore, decrease with increasing concentration until it becomes vanishingly small for the saturated solution. This decrease in interfacial tension would explain why the experimentally measured surface tension of a solution continues to alter with increase of concentration even after a monomolecular film is formed on the surface, and predicts a definite value toward which surface tension should tend with approach to saturation.

Using the du Noüy tensimeter (inaccurate for such systems) for *p*-toluidine solutions near saturation it was found that within the experimental error the solutions attained a constant value of surface tension. Three solutions containing 5.6, 6.0 and 6.4 g. of toluidine per liter gave each a surface tension of 52.6 dynes. It is interesting to note that the so-called Gibbs theorem would predict zero adsorption for these solutions, whereas the actual adsorption is the same as for the more dilute solutions where the surface tension is changing rapidly with concentration.

It is interesting to speculate as to the depth to which a surface really extends, that is, the depth to which it is different in properties or in concentration from the bulk of the liquid. One has to avoid the dilemma that on the one hand the range of molecular attraction extends only between molecules actually in contact and on the other that the composition of the layer immediately below the monomolecular film is different for each concentration of the solution as is shown by the change in surface tension with change in concentration. We have found that the total weight of excess toluidine associated with one square centimeter of surface is 14×10^{-8} g. Of this possibly 8×10^{-16} g. are in the monomolecular film of pure *p*-toluidine, leaving 6×10^{-8} g. in the adjacent submerged region. Since a saturated solution of *p*-toluidine contains only 6 g. per liter, 6×10^{-8} g. would in itself suffice to saturate a depth of 1×10^{-8} sq. cm., which is what was formerly regarded as within the range of direct molecular attraction. However, since the solution itself already contains anywhere from a few grams up to saturation amount of *p*-toluidine per liter, and this adsorption is additional and constant for all except the most dilute solutions, there is more toluidine concentrated below the surface than could be contained in a saturated solution. However, we do not conceive of these underlayers as supersaturated or even as uniform but explain them in accordance with Fig. 1d as due to the presence of

the chains of *p*-toluidine reaching down deeply into the solution from various isolated points on the under side of the monomolecular layer.

Test of the So-Called Gibbs Theorem $\Gamma = \frac{-c}{RT} \frac{d\sigma}{dc}$

All authors previous to 1925 did not use the true Gibbs theorem but substituted for it the simplified approximation formula given in the heading above in which adsorption is merely referred to as change of surface tension with concentration. Now that we have substantially accurate quantitative results, it is possible to show that this is inadmissible even for the simple crystalloidal substances we have used, namely, toluidine, amyl alcohol and camphor in aqueous solution.

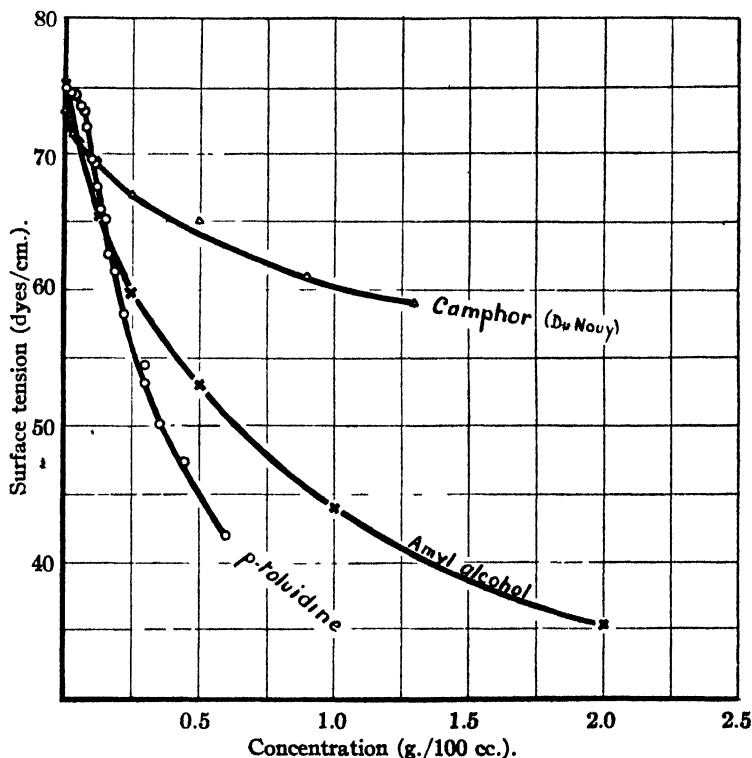


Fig. 3.—Surface tension of aqueous solutions of *p*-toluidine and amyl alcohol carefully measured by the Ferguson method and of camphor using du Nouy tensimeter.

Special care was devoted by P. R. Edwards to obtaining trustworthy values for the surface tension of aqueous solutions of *p*-toluidine. He employed the Ferguson method in which the pressure of air is measured which is required to blow down into a capillary tube inserted in the surface of a solution until the meniscus in the capillary is flat and exactly at the

lower end of the capillary.¹³ Fig. 3 gives the data obtained by Edwards for solutions of *p*-toluidine, each point being the mean of six readings. Fig. 3 shows also Edwards' values for aqueous amyl alcohol by the same method and our values for aqueous camphor¹⁴ using the du Noüy tensiometer with the procedure suggested by Klopsteg.¹⁵ Hence, the values for camphor can only be regarded as semi-quantitative, although consistent.

In calculating the slope of the surface-tension curves it has to be remembered that the slope is not obtained by direct measurement but by the difference in values of isolated measurements of the surface tension itself, that is, small differences between large numbers. However, this source of error is completely eliminated if the comparison of slope with observed adsorption is not confined to a single point but is spread out over a wider range of concentrations.

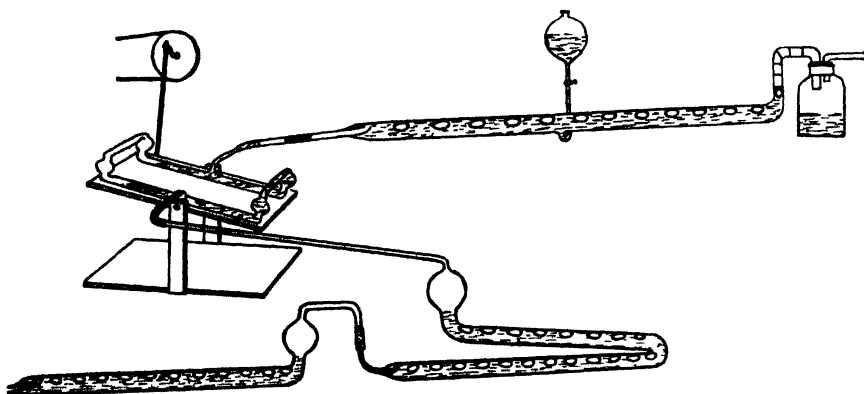


Fig. 4.—The apparatus employed for the measurement of absolute adsorption in the air-water interface.

In Table IV are given the values calculated by the concentration formula $\Gamma = \frac{-c}{RT} \frac{d\sigma}{dc}$ from the slope of the surface tension curve for comparison with the adsorptions actually observed, $R = 7.843 \times 10^{-8}$ ergs per g. The comparison is still more strikingly made in Fig. 4.

It is evident that although the predictions of the concentration formula are of the right order of magnitude it can only be regarded as being semi-quantitative. The same conclusion results from the fairly good experiments with amyl alcohol and the less exact experiments with solutions

¹³ (a) Edwards, *Trans. Faraday Soc.*, 16, 384 (1921); (b) *J. Chem. Soc.*, 127, 744 (1925).

¹⁴ Although Edwards has published careful measurements of aqueous solutions of camphor his recorded concentrations should be divided by 10 and hence all his solutions are more dilute than those here used.

¹⁵ Klopsteg, *Science*, 60, 319 (1924).

TABLE IV

COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED ADSORPTION OF *p*-TOLUIDINE

Concn. ^a	0.6	1.0	1.4	2.0	3.0	4.0	5.0
Slope ^b	55000	106000	106000	76810	51210	34000	32800
"Gibbs"	1.5	4.7	6.6	6.8	7.1	7.3	7.5
Observed	2.4	6.5	10.4	12.7	13.4	13.2	13.0

^a Concn. in g. of *p*-toluidine per liter of solution.^b $d\sigma/dc$ in c.g.s. units.

of camphor now to be described. In all cases we are dealing with crystalloidal non-electrolytes. Hence, the concentration formula must be regarded as only a first approximation.

The Adsorption of Amyl Alcohol and of Camphor in the Air-Water Interface

Iso-amyl alcohol supplied by Kahlbaum and distilling at 130° was employed. On account of its appreciable volatility great care was taken to have the nitrogen passed through the aqueous solution exactly saturated so that when no bubbles or films were allowed to leave the main reservoir the passage of the nitrogen caused no detectable alteration in the concentration of the solution. One division of the interferometer scale corresponded to 3.7×10^{-6} g. per cc. The results of the measurements have been collected in Table V. The values for the most dilute solutions are only approximate because of the small analytical change; amyl alcohol does not affect the refractive index nearly as much as toluidine. The same apparatus was used in all experiments.

TABLE V

ABSOLUTE MEASUREMENTS OF THE ADSORPTION OF AMYL ALCOHOL IN THE SURFACE OF ITS AQUEOUS SOLUTION^a

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.) uncorr. corr.		Cc. of film soln.	$\Gamma \times 10^{-3}$ obs. g./sq. cm.
0.5	0.98	11000	3	3	42	4
	1.14	11000	3	3	46	3
	0.82	9400	3	3	44	5
	0.89	9100	3	3	44	5
					Mean =	5
1.0	1.55	9900	4	5	44	8.2
	0.78	9680	4	5	48	9.2
	.72	9930	4	5	44	8.2
	.78	9600	4	5	44	8.5
					Mean =	8
1.5	0.86	9300	6	7	46	13
	.76	9800	7	8	38	12
	.96	11600	7	8	45	11
	.82	9400	6	7	44	12
					Mean =	12

TABLE V (Concluded)

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film, soln.	$\Gamma \times 10^{-8}$ obs. g./sq. cm.
			uncorr.	corr.		
2.0	0.71	7600	7	8	40	15.6
	.86	10700	10	11	40	15.2
	.76	10600	9	10	44	15.4
	.97	7320	7	8	43	17
					Mean =	16
3.0	0.73	10000	9	11	41	17
	.79	10400	10	11	41	16
	.73	10000	10	11	39	16
	.65	10500	10	11	41	16
					Mean =	16
5.0	0.72	10900	10	12	42	17.1
	.57	11200	9	11	42	15.2
	.54	11600	13	15	34	16.2
	.56	11500	11	12	42	16.4
	.66	12000	9	11	45	15.2
	.48	12250	11	13	37	15
					Mean =	16

* Time of contact of nitrogen and solution varied between 12 and 15 seconds.

A constant value for the adsorption, namely, 16×10^{-8} g./sq. cm. is attained at and above the concentration of 2 g. per liter. This corresponds to one molecule of amyl alcohol for each 9×10^{-16} sq. cm. of surface. Langmuir found that the normal higher insoluble alcohol, hexadecyl alcohol, had an area in monomolecular film of 2×10^{-16} sq. cm. Hence, once more the observed adsorption is definitely greater than the amount which could be accommodated on the surface as a close-packed monomolecular film.

The experiments with camphor are more difficult because of the instability of the bubbles. Hence, a continuous flow of liquid was maintained over the bend at the top of the vertical tube. The camphor used was the best procurable natural Japanese, melting at 177° . One division of the interferometer reading corresponded to 2.7×10^{-6} g. per cc. The results are collected in Table VI.

It will be noted that for solutions whose concentration ranges from 0.5 to 1.3 g. per liter (saturated solution) the adsorption is approximately 10×10^{-8} g. per sq. cm., corresponding to an area of 23×10^{-16} sq. cm. per molecule of camphor.

Tables VII and VIII give the values predicted from the approximate Gibbs concentration theorem for comparison with the observed amounts of adsorption. The data are also given in Fig. 4 showing that the discrepancy is of the same order of magnitude, and in the same direction as in the case of toluidine.

TABLE VI
ABSOLUTE MEASUREMENTS OF THE ADSORPTION OF CAMPHOR IN THE SURFACE OF ITS
AQUEOUS SOLUTION

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film soln.	$\Gamma \times 10^{-3}$ obs. g./sq. cm.
0.25	1.37	7800	3	4	43	6
	0.86	9300	3	5	42	6
	1.30	6600	2	3	41	5
	0.96	8800	3	4	40	5
					Mean =	6
0.50	1.12	8300	4	6	50	10
	1.92	7000	3	5	50	10
	0.91	8200	3	5	50	8
					Mean =	10
0.90	0.92	9000	5	8	43	10
	.86	9300	5	9	47	12
	1.00	8600	4	8	44	11
	0.82	9400	6	9	47	12
	.99	8700	5	9	43	12
					Mean =	11
1.3	0.73	10000	6	9	42	10
	.93	8900	5	8	43	11
	.97	8800	6	8	44	11
	.89	9100	6	8	40	10
	.82	9400	6	9	42	11
					Mean	11

TABLE VII
COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED
ADSORPTION OF AMYL ALCOHOL

Concn. ^a	Slope ^b	"Gibbs"	Observed
0.5	7700	1.4	5
1.0	6299	2.3	8
1.5	4919	2.7	12
2.0	4249	3.1	16
3.0	3060	3.3	16
5.0	2250	4.1	16
10.0	1350	4.9	

^a Concentration in g. per liter.

^b $d\sigma/dc$ in c.g.s. units.

TABLE VIII
COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED
ADSORPTION OF CAMPHOR

Concn. ^a	Slope ^b	"Gibbs"	Observed
0.25	12400	2	6
.50	9800	3	10
.90	7400	4	11
1.3	5000	4	11

^a Concentration in g. per liter.

^b $d\sigma/dc$ in c.g.s. units.

Since the error in the concentration formula is evidently several fold, this explains the results obtained by Langmuir and later workers who in lieu of actual experiment used this formula to obtain values for the adsorption of one molecule of a lower fatty acid for 31×10^{-16} sq. cm. of surface, whereas one molecule can only cover 22×10^{-16} sq. cm. in a complete monomolecular film and presumably the true adsorption is still greater. We hope to present experimental evidence in a further communication. The conclusion is that we must go back to the true equations as actually formulated by Gibbs.

Adsorption and Thermodynamics

The glaring discrepancy between adsorption as actually observed and the predictions of the simplified so-called Gibbs formula $\Gamma = (-c/RT) \cdot (d\sigma/dc)$ makes it necessary to examine the basis upon which the thermodynamic treatment of this subject rests.

The derivation given by Lewis and Randall¹⁶ shows clearly the assumptions now usually made. These are that (1) only two components are present anywhere in the system, and that (2) the only free energy of a surface is its surface tension multiplied by its area. If so, necessarily $\Gamma = -(d\sigma/d\mu)$, where μ is the potential of Gibbs.¹⁷ This may be written $\Gamma = -d\sigma/d\bar{F}$ or $\Gamma = (-a/RT)(d\sigma/da)$ where \bar{F} and a are the partial molal free energy and activity of the solute in Lewis and Randall's nomenclature.

The formula is usually simplified by substituting concentration for activity, with the misleading results which we have previously discussed.

One reason for the disagreement between the facts and the simplified formula is due to the nature of the materials usually chosen. Surface-active substances are usually far from ideal and often of limited solubility, with corresponding deviation from the ideal partial vapor pressure. It should be clearly understood that the potential or activity is that exhibited by the solute in the bulk of the solution and it is not affected by whatever complications occur at the surface; the whole behavior at the surface is governed by the potential within the ordinary homogeneous solution, and the potential of each component in the surface must equal this, no matter how complicated the actual surface may be. For example, a crystalloidal solute might be adsorbed in colloidal form, but its amount would still be that predicted from the properties of the bulk of the solution; however, a solute which was so readily brought into colloidal form would be expected to possess a potential or activity differing from that of an ideal solution.

Reverting to the thermodynamic formulation, the first consideration

¹⁶ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 250.

¹⁷ In the notation used by Lewis and Randall, $v_1 = (-d\gamma/d\bar{F}_1)_\sigma$.

that arises is that seldom or never have true, two component systems been actually under observation, although this is fundamental. Solutions of electrolytes or substances capable of hydrolysis, such as soap, cannot be treated as two component systems except in the rare event that the composition of the adsorbed material is identical with that of the solute remaining in the solution. For example, the foam from a neutral soap solution contains acid soap; thus the free alkali remaining in the solution is introduced as a new and important variable component. The numerical data for the adsorption of soap will be dealt with in a later paper; they present the most flagrant conflict with the prediction of the simplified formula, differing in order of magnitude and even in sign.

The component (or components) actually present, but hitherto ignored, is the gas (or air) in presence of which the surface tension is measured and bubbles are produced. For the more general treatment it is simplest to proceed from the original equation. In this subject, number 508 of Gibbs (Scientific Papers, page 230). Gibbs' equation 508 is an application of the first law of thermodynamics, and reads $d\sigma = -\eta_s d\ell - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3$, etc., where the subscripts refer to the respective components (for example, Γ_1 water, Γ_2 toluidine and Γ_3 the nitrogen); the first term on the right vanishes for constant temperature. The equation implicitly excludes electrical, etc., effects. It makes the same assumption that the free energy of the surface is given by its surface tension multiplied by its area, but it explicitly mentions each component present in the system. The adsorptions Γ , here referred to by Gibbs are the absolute values, defined as the excess or deficiency of the amount of each component as compared with that which would have been present if the two homogeneous phases (solution and vapor) had extended without alteration up to an arbitrary mathematical dividing surface. This ingenious definition affords a definite value for the adsorption, no matter how deep, stratified or complicated the actual physical surface may be.

The value of Γ for any one component (preferably the solvent) may be set equal to zero by suitably placing the arbitrary mathematical surface. This may be done even if the solvent is actually absent from a layer of the physical surface, as is the case where we have a monomolecular film of solute upon the surface, with solution below and vapor above it. Having set $\Gamma_2 = 0$, the values of Γ_2 and Γ_3 are defined with reference to the solvent. The experiments described correspond with this definition, because they are so carried out that the vapor phase is kept unaltered as the surface is destroyed, and hence the whole of the material in the physical surface goes into the final liquid which is then analyzed for change in concentration relative to the solvent. Lewis and Randall's definition is the same, for they keep the total amount of solvent in the system constant and define Γ_2 as the amount of the second component it is necessary to add when the

surface is increased if the bulk of each phase is to be kept unaltered in properties, such as partial molal free energies, and hence in concentration.

Where there are second and third components (such as *p*-toluidine and nitrogen) their adsorption is $\Gamma_2 = -(\partial\sigma/\partial\mu_2)_{\mu_1}$ and $\Gamma = -(\partial\sigma/\partial\mu_3)_{\mu_1}$, each of which is readily measured, although this has never been done. It is obvious that the two adsorptions will mutually interfere. The gas cannot be quite ignored. For example, it has been stated that the surface tension of mercury is 10% lower in the presence of one atmosphere of nitrogen than *in vacuo*; similarly, nitrogen lowers the surface tension of water by about 1%, which would correspond to the adsorption of about 3% as many molecules of nitrogen as of *p*-toluidine. However, such mutual interference cannot explain the high values of the observed adsorptions.

Several authors such as Donnan⁷ have suggested that the Gibbs theorem applies only to a layer of the surface one or two molecules deep, and that other changes may occur in deeper layers which are not included in the Gibbs equation. This is to forget the strict definitions of Gibbs who in introducing his thermodynamic formula found it essential to include with the surface a layer of the adjacent phases so deep that the boundaries reached into the truly homogeneous phases on both sides. The Gibbs effect is, therefore, the sum total of all concentration changes whether one or very many molecules in depth from the surface.

In the Gibbs equation all electrical effects are expressly excluded. Nevertheless, all surfaces are electrified in that they exhibit electrophoresis, and this is just as prominent in the gas-liquid interface as in any other. Hence, it is necessary to add at least one term (namely, $-edV$, where e is charge and V is electrical potential) to Gibbs' equation even for dealing with surfaces of non-electrolytes. If ions in solution (such as H^+ and OH^-) are not adsorbed in absolutely identical amounts, this in itself adds one more component to the system. The term $-edV$ produces the equation $d\sigma = -edV$ used by Lippmann¹⁸ before Gibbs, when the temperature and the chemical potential are held constant, which is easily done if the composition and electrical potential of the vapor phases are kept constant.

The exact formulation is not quite simple because of the depth and complex structure of the surface layers. For example, Freundlich has demonstrated that the layer in which movement takes place exhibits an electrokinetic potential which bears little or no relation to the total difference in potential of the two homogeneous phases. Hence, the surface is far from behaving as a simple electrical condenser as envisaged by the earlier investigators. This, however, accords with the recent recognition of the fact that the total surface energy of a liquid is not defined entirely by the nature and orientation of the outermost monomolecular layer of

¹⁸ Lippmann, *Ann. chim. phys.*, (V) 5, 494 (1875).

molecules or ions. Great uncertainty exists as to the value or values of the potential difference between phases involving non-electrolytes. It is chiefly a matter of convention¹⁹ that they are usually taken to be between 20 and 50 millivolts, and such experiments as those of Frumkin give values over ten times greater. Even the absolute charges may not be entirely negligible, as is shown by the behavior of thunder clouds in which mere coalescence of drops and diminution of air-water surface produces discharges of the order of one hundred million volts.

A further communication will deal with thermodynamic data for solutions of *p*-toluidine. The experiments here recorded were completed at Bristol University, England, in 1925.

Summary

1. A simple method has been devised for accurately measuring the absolute adsorption at an air-liquid interface and for the first time trustworthy quantitative data have been obtained. Aqueous solutions of *p*-toluidine, amyl alcohol and camphor have been studied.

2. In every case the amounts actually adsorbed are several times greater than that corresponding to a monomolecular film and it is, therefore, concluded that for these solutions of ordinary non-electrolytes over a wide range of concentration of solutions the surface consists of a saturated monomolecular film of solute resting upon a comparatively thick layer of concentrated solution, gradually falling off with depth to the bulk concentration of the solution.

3. The mechanical explanation of this structure is that chains of oriented molecules extend downwards into the solution from the outermost monomolecular film. It is not assumed that there is a wide range of molecular attraction but rather that in effect the same result is produced by chains of contiguous molecules. It was found that many lines of evidence are in agreement with this hypothesis.

4. The so-called concentration formula of Gibbs, as usually quoted, is shown to give erroneous values for adsorption. It is necessary to use the true thermodynamic formula of Gibbs and not only to take into account all the components (usually much more numerous than anticipated) but also to include the electrical effects which universally occur at surfaces but which were not included in the Gibbs equation. Hence, the numerous data which have been calculated by means of the Gibbs concentration formula are shown to be in error.

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¹⁹ See *J. Phys. Chem.*, 28, 706 (1924).

NOTES

A Convenient Thermostat Heater.—A dependable thermostat heater that does not emit any light, that is perfectly insulated from the bath and that does not corrode and render the water turbid, became necessary in the work of the author. The usual lamps and metallic heating coils failed to meet one or more of these requirements. A capillary thread of mercury worked very successfully on an A. C. line stepped down by a toy transformer, but it was found impractical to make a mercury resistance high enough to go across a 110-volt D. C. line directly. Accordingly, a new heater had to be developed.

The following device met all these needs very satisfactorily. A Pyrex tube about 40 cm. long and 3 mm. bore was bent into a U and filled with fine flake graphite packed tightly by tapping. Contact was made by means of pieces of copper rod, the ends of which were turned down to conical points to increase the area of contact with the graphite and which were held in place by means of spring leads from the binding posts as indicated (see Fig. 1). A heater of these approximate dimensions, now in use, was found to have a resistance of 270 ohms and accordingly has a heating capacity of 45 watts when put on the 110-volt line. On testing the regulation with a Beckmann thermometer, the heater was found to go on and off regularly in an interval of 0.012° . It would be difficult to distribute this lag between the lag of the heater, the stirring, or the sensitivity of the mercury regulator used. In any case, as this degree of regulation was quite ample for the work in hand, no attempt was made to improve it.

This graphite heater is easily made, has given excellent service under the conditions indicated above, and should find application wherever a heater fulfilling these requirements is desirable.

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Fig. 1.

The Computation of Partial Molal Quantities of Binary Solutions.—The method here developed will be particularly useful in those cases in which great accuracy is desired. For a general discussion of partial molal quantities and methods of their calculation the reader is referred to the work of Lewis and Randall.¹

¹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

Let G be any extensive property of a system consisting of n_1 moles of A and n_2 moles of B. The mole fraction, N_1 , of constituent A is $n_1/(n_1 + n_2)$, and similarly for N_2 . The molal value, G , of an extensive property of the system is by definition

$$G = G/(n_1 + n_2) \quad (1)$$

The corresponding molal quantities of the pure constituents are obtained by equating n_2 or n_1 to zero, respectively. Let us note that

$$n_1 = N_1 n_2 / N_2 \quad (2)$$

The variation of the molal values may be considered as due solely to the change in the number of moles of one of the constituents, the amount of the second constituent being considered constant. Differentiating Equations 1 and 2, respectively, we obtain

$$(dG)_{n_2} = G dn_1 + (n_1 + n_2) dG \quad (3)$$

$$dn_1 = n_2 dN_1 / N_2^2 \quad (4)$$

By definition

$$\bar{G}_1 = dG/dn_1 \quad (5)$$

$$= G + (n_1 + n_2) dG/dn_1 \quad (6)$$

We will now define a new function,

$$\Delta = G - (N_1 \bar{G}_1 + N_2 \bar{G}_2) \quad (7)^2$$

from which

$$dG = d\Delta + \bar{G}_1 dN_1 + \bar{G}_2 dN_2 \quad (8)$$

Substituting the values of G and dG from Equations 7 and 8 into Equation 6 and simplifying,

$$\bar{G}_1 = G_1 + \Delta + N_2 \frac{d\Delta}{dN_1} \quad (9)$$

By means of Equation 9 we may obtain the partial molal quantities from the directly measured molal quantities and a correction term that is small

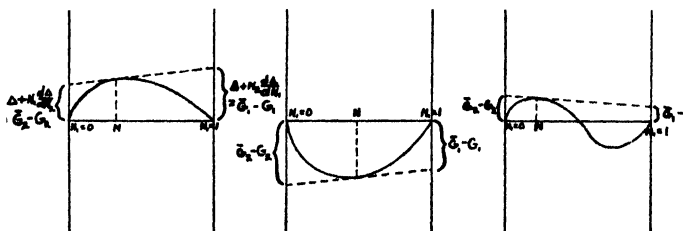


Fig. 1.

for all solutions that are approximately perfect. The graph of Δ , calculated from the directly measured molal quantities against mole fraction, will in general have one of the following three forms (Fig. 1). (From its definition Δ will be zero for $N = 0$ or 1.) The intercept of the tangent to the curve on the axis of the pure constituent is the difference between the partial molal value and the molal value for the constituent chosen at the

² In certain cases it may be desirable to take an arbitrary constant in place of G_2 .

mole fraction of the point of tangency. This is indicated in the above diagrams.

An accuracy greater than the practicable limit of the previous method may be obtained by the following continuation, if the accuracy of the original data is sufficient to warrant it. Let $y = f(N)$ be an analytical curve which fits that of $\Delta = f(N)$ fairly closely. Treating the deviation $\Delta' = \Delta - y$, in the same way as before, we obtain the equation

$$\bar{G}_1 = G_1 + (y + N_2 dy/dN_1) + (\Delta' + N_2 d\Delta'/dN_1) \quad (10)$$

Equation 10 gives the partial molal value as the sum of the directly measured molal value, a readily computed term, and a quantity which as before can be obtained graphically.

CONTRIBUTION FROM THE CHEMICAL
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BENJAMIN SOSNICK

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The Saponification of Ethyl Acetate.—It was found that F. Thomas¹ had reported that the velocity of saponification of ethyl acetate by barium hydroxide in aqueous solution is influenced by light. Although the data reported seemed too inaccurate for acceptance, it was desired to ascertain if such variation of intensity of light as may be expected in a laboratory illuminated by diffuse daylight has any effect on the rate of hydrolysis of ethyl acetate in aqueous sodium hydroxide solution. Accordingly, measurements were carried out by me as follows. The technique and apparatus described in a previous paper² were used except that in the first experiment and in each alternate experiment thereafter, the container of the reaction mixture was wrapped in tin foil and the operations of mixing the reagents and of removing the samples of the mixture for analysis were carried out with a dim ruby lamp as the only source of illumination. The respective concentrations of ester and sodium hydroxide were 0.008 and 0.01. The average coefficient found for the reaction in darkness (ten experiments) was 6.77 at 25.00°. The average (eight experiments) for the reaction in diffuse daylight was also 6.77 at 25.00°. It was, therefore, established that variations of intensity of diffuse daylight such as may occur under varying laboratory conditions have no effect on the rate of the reaction in question.

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¹ Thomas, *Diss.*, Freiburg i/Br., Speyer and Kraener, 1908.

² Terry and Stieglitz, *This Journal*, 49, 2216 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE,
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UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS

I. THE CONSTITUTION OF 2-KETO-11-UNDECYLIC ACID

BY WILLIAM WHALLEY MYDDLETON AND ARTHUR WILLIAM BARRETT

RECEIVED APRIL 28, 1927

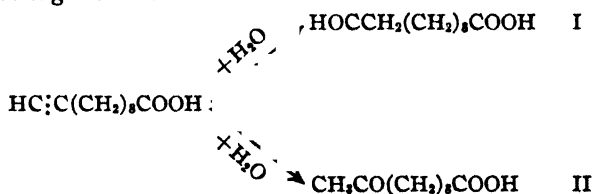
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The preparation of a keto-undecylic acid has been described by Welander.¹ It was obtained by the action of moderately concentrated sulfuric acid upon 9,10-undecinoic acid. The constitution of the latter is fixed by the fact that it yields azelaic acid on oxidation,² so that Welander's ketonic acid might be either $\text{CH}_3\text{CO}(\text{CH}_2)_8\text{COOH}$ or $\text{CH}_3\text{CH}_2\text{CO}(\text{CH}_2)_7\text{COOH}$.

The constitution might have been settled by submitting the oxime to the Beckmann transformation and proceeding in the manner described by Baruch,³ but Welander failed to effect the Beckmann transformation.

We set out to determine the constitution in a different way, anticipating that the same acid would be obtained by starting with 10,11-undecinoic acid described by Krafft² and called by him dehydro-undecylenic acid. We found that when this acid was treated with sulfuric acid in the manner described by Welander a poor yield of a keto-undecylic acid was obtained melting at 59.5° and forming an oxime melting at $68-69^\circ$.

The constitution of ethyl dehydro-undecylenate is known from the fact that it forms a silver acetylide with alcoholic silver nitrate and the free acid yields sebacic acid on oxidation.² The ketonic acid derived from dehydro-undecylenic acid must therefore be produced by the second of the two following reactions.



No distinctive aldehydic reactions were found for the product or in its ethyl ester.

Welander gives the melting point of his keto-undecylic acid as 49° and describes its oxime as a non-crystallizable oil. It appeared from this that his must be 3-keto-11-undecylic acid.

We then devised a method of preparing the ketonic acid from dehydro-undecylenic acid in better yield. The acetylenic acid was dissolved in

¹ Welander, *Ber.*, 28, 1449 (1895).

² Krafft, *Ber.*, 29, 2232 (1896).

³ Baruch, *Ber.*, 27, 172 (1894).

glacial acetic acid and was warmed on the water-bath at 70° with mercuric acetate. During about five hours a small amount of mercurous acetate separated and was filtered off. The solution was poured into twice its volume of water and a solid separated. Recrystallization from dil. acetic acid gave a product of definite composition in the form of microcrystalline, colorless needles.

Analysis showed the crystals to be the mercuric salt of a triacetoxymercuri-keto-undecylic acid. Treatment with moderately concd. hydrochloric acid gave a quantitative yield of the keto-undecylic acid melting at 59.5°. To obtain good yields from the dehydro-undecylenic acid it was found unnecessary to isolate the mercury compound, but the whole of the acetic acid solution was treated with mineral acid and the mixture then poured into water.

The analysis of the mercury compound was carried out in three stages. The mercury was estimated by precipitation as mercuric sulfide, hydrogen sulfide being passed through an acetic acid solution containing a weighed amount of the substance. The acetoxy group was determined on a quantity of the substance, dried for several days in a vacuum desiccator at the pump, by suspending a weighed amount in lime-dried absolute alcohol and distilling from a water-bath after addition of concd. sulfuric acid. Ethyl acetate was estimated in the distillate by quantitative hydrolysis. The keto-undecylic acid was liberated from a third quantity by hydrochloric acid, extracted with ether and weighed.

The analyses fix the constitution as $(\text{CH}_3\text{COOHg})_3\text{C.CO}(\text{CH}_2)_8\text{COO}(\text{Hg})^{1/2}$.

We then attempted to prepare Welander's ketonic acid from 9,10-undecinoic acid by the intermediate formation of a mercuric compound. The product gave analyses for the mercuric salt of a diacetoxymercuri-keto-undecylic acid. Treatment with hydrochloric acid gave a ketonic acid which melted at 49–50°. This appeared to be Welander's acid which melted at 49°. Systematic recrystallization from petroleum ether (b. p. 60–80°) led to the isolation of two pure ketonic acids having the molecular formula $\text{C}_{11}\text{H}_{20}\text{O}_3$, one melting at 59.5° identical with that prepared from dehydro-undecylenic acid, and the second melting at 43.5°. The first was obtained in fair amount but less than 1 g. of the second was isolated after recrystallization 18 times. The original 9,10-undecinoic acid melts at 59.5° but analysis and the melting point of a mixture (45–50°) showed that the two substances melting at 59.5° were not identical.

We then repeated Welander's preparation by means of sulfuric acid and obtained a product melting at 48–49°. On repeated systematic recrystallization from petroleum ether we were again able to separate two ketonic acids melting at 59.5 and 43.5° in roughly the same proportions.

It still remained to show that the predominating high-melting con-

stituent in the mixture did not result from the presence of dehydro-undecylenic acid in the 9,10-undecylenic acid used, since both of these acetylenic acids are prepared by the action of potassium hydroxide upon 1,2-dibromo-11-undecylenic acid² at different temperatures. Our next step was therefore to prepare pure specimens of the ethyl esters of the two acetylenic acids by repeated fractionation in a vacuum. Ethyl dehydro-undecylenate is precipitated from alcoholic solution as a silver acetylide by adding alcoholic silver nitrate, and we found that any quantity of this ester greater than 1% present in admixture with ethyl 9,10-undecylenate could be detected by the formation of a precipitate in this reaction.

A quantity of ethyl 9,10-undecylenate which failed to show turbidity with silver nitrate was dissolved in glacial acetic acid and treated with mercuric acetate. The mercury compound was isolated as before. It gave analyses for the ethyl ester of a diacetoxymercuri-keto-undecylenic acid, $(\text{CH}_3\text{COOHg})_2\text{C}_{10}\text{H}_{17}\text{OCOOC}_2\text{H}_5$.

Hydrochloric acid liberated an ester which was separated into two fractions by distillation under diminished pressure. The higher-boiling fraction, distilling at 169–170° (corr.) (12 mm.), represented about 50% of the original ester and gave on hydrolysis the ketonic acid melting at 59.5°. The lower-boiling fraction appeared with progressive rise in temperature from 158 to 169° and gave on hydrolysis a mixture from which a further amount of the acid melting at 59.5° and a small amount of that melting at 43.5° were separated by crystallization from petroleum ether.

On the evidence so far obtained, the acid melting at 59.5° must be 2-keto-11-undecylenic acid and that melting at 43.5° 3-keto-11-undecylenic acid.

We have succeeded in submitting the oxime of the former to the Beckmann transformation under the influence of concd. sulfuric acid. When the product was heated in a sealed tube with concd. hydrochloric acid it yielded almost the calculated amount of sebacic acid.

Experimental Part

Preparation of 1,2-Dibromo-11-undecylenic Acid.—Petroleum ether (b. p. 60–80°) was treated with excess of bromine at room temperature and the mixture allowed to stand for two days. It was then washed with a solution of sodium bisulfite and dried. After distillation the purified product was used as solvent. One hundred and seventy g. of undecylenic acid (m. p. 24.5°; b. p. 168.3° at 15 mm.) was dissolved in 500 cc. of purified solvent. One hundred and fifty g. of bromine was added during one and one-half hours while cooling in a mixture of ice and salt. When about three quarters of the bromine had been added the dibromo acid began to separate. Efficient stirring was required from this point. When the whole of the bromine had been added the mixture was allowed to stand for an hour. The precipitate was filtered off at the pump and washed with 100 cc. of cold petroleum ether. The cake was broken up and transferred to a vacuum desiccator and the excess of bromine and solvent was removed during 24 hours. The white crystals melted at 38.5°; yield, 250 g. The rest of the dibromo derivative was obtained as an oil after washing the filtrate with a solution of sodium

bisulfite, drying and evaporating. The yield of oil was approximately the same in a number of brominations.

Anal. Calcd. for $C_{11}H_{20}O_2Br_2$: Br, 46.5; equiv. wt., 344. Found: Br, 46.2; equiv. wt. (titration against standard alkali), 345.1.

Preparation of Dehydro-undecylenic Acid and 9,10-Undecynolic Acid.—Dehydro-undecylenic acid was prepared from the dibromo acid by the method of Krafft.³ The constants of the substance given by this author were confirmed. 9,10-Undecynolic acid was obtained from the dibromo acid by the method of Welander.¹ The constants described by Welander were confirmed.

Conversion of the Acetylenic Acids into Esters.—The method of esterification at first employed was that described by Krafft³ in which the acid is boiled under a reflux condenser with alcohol and an excess of potassium carbonate. The filtered solution containing the potassium salt was heated in pressure bottles with excess of ethyl iodide. Finally it was found to be less troublesome to reflux the acid with ten times its weight of lime-dried absolute alcohol and its own weight of concd. sulfuric acid. The mineral acid was mixed with the alcohol and the acetylenic acid added when cold. The solution was allowed to stand at room temperature before refluxing for ten hours. At the end of this time the solution was cooled and ether added. After shaking with water the ethereal solution was separated, washed with dil. sodium carbonate solution and water, dried and evaporated. The residue after distillation of the ether was fractionated under diminished pressure. The esters were collected at the following temperatures: ethyl dehydro-undecylenate, 145° (15 mm.), and ethyl 9,10-undecynolate, 197° (49 mm.).

Small quantities of the pure esters were hydrolyzed and gave the following acids: dehydro-undecylenic acid, m. p., 43° ; 9,10-undecynolic acid, m. p., 59.5° .

Treatment of Dehydro-undecylenic Acid with Mercuric Acetate.—Ten g. of dehydro-undecylenic acid was dissolved in 25 cc. of glacial acetic acid in a 500cc. flask fitted with an air condenser. To this was added a solution of 39 g. of mercuric oxide in 225 cc. of glacial acetic acid. The flask was heated on the water-bath at 70 to 100° for five hours. At the end of this time the deposit of mercurous acetate was filtered off while hot and the solution cooled and poured into 250 cc. of water. The solid which separated was filtered off and recrystallized from 75% acetic acid. The colorless microcrystalline needles were drained at the pump, dried on filter paper and finally washed with ether and dried in the vacuum desiccator for at least two days on the pump. There were obtained about 1.5 g. of mercurous acetate and 45 g. of the mercuric compound.

Treatment of 9,10-Undecynolic Acid with Mercuric Acetate.—Ten g. of the acetylenic acid treated as in the preceding case with 28 g. of mercuric oxide in 250 cc. of glacial acetic acid gave a small amount of mercurous acetate and 37 g. of the mercuric compound in colorless, microcrystalline needles.

Treatment of Ethyl 9,10-Undecynolate with Mercuric Acetate.—Thirty-three g. of the ethyl ester which gave no precipitate with alcoholic silver nitrate was treated as described above with 70 g. of mercuric oxide in 500 cc. of glacial acetic acid. About 4 g. of mercurous acetate was separated, and on pouring the filtrate from this into water the product separated as a thick, amber-colored, viscous oil which solidified when shaken with water. The solid crystallized from 75% acetic acid in the form of fine needles; yield, 95 g.

Treatment of Ethyl Dehydro-undecylenate with Mercuric Acetate.—Thirty g. of the ester was treated in 600 cc. of glacial acetic acid with 95 g. of dissolved mercuric oxide. The procedure was the same as that described above.

Analysis of the Mercuric Compounds

1. **Estimation of Mercury.**—Approximately 0.5 g. of the substance was dissolved in hot glacial acetic acid and the solution saturated with

hydrogen sulfide. Concd. hydrochloric acid was then added and the precipitated mercuric sulfide filtered through a Gooch crucible, washed with ether, dried and weighed.

2. **Estimation of Acetoxy Group.**—Approximately 1.5 g. of the substance was weighed and transferred to a distilling flask, the side tube of which was bent downwards at the middle of its length to make an angle of 120° . The flask was fitted with a dropping funnel and was attached to a Liebig condenser. Fifty cc. of absolute alcohol (lime-dried) mixed with 10 cc. of concd. sulfuric acid was admitted through the funnel and the flask was then heated on the water-bath and wrapped round with a duster. The distillate was collected in excess of standard 0.5 *N* alcoholic potassium hydroxide solution, and dry absolute alcohol was dropped into the flask at the same rate as that of the distillation. Fifty cc. of alcohol was added in this way and then the contents of the flask were allowed to distil to about 30 cc. The distillate was refluxed for 40 minutes and the excess of alkali titrated with 0.5 *N* acid. After each titration the solution was evaporated almost to dryness. One portion was treated for the recognition of potassium acetate and the second was diluted with water and acidified to ascertain that no turbidity appeared.

3. **Estimation of the Ketonic Acid or Ester Liberated by Treatment with Hydrochloric Acid.**—Approximately 5.0 g. of the substance was warmed with moderately concd. hydrochloric acid and the mixture then diluted with water. Esters were shaken in a flask with dil. acid, cold. No precipitate of mercurous chloride formed. The ketonic compound was extracted with ether and weighed after being washed and the solvent distilled. The residue was dried before weighing by adding a few drops of absolute alcohol and blowing out the flask at the bellows while immersed in boiling water. Two or three treatments in this way served

TABLE I
RESULTS OF THE ANALYSES

Initial acetylenic compd.	Analysis of mercuric compound		
	Hg, %	CH ₃ COO, %	Ketonic compd., %
Dehydro-undecylenic acid, found	65.2	16.3	18.5 C ₁₁ H ₂₀ O ₂
Calcd. for mercuric 1-triacetoxy-mercuri-2-keto-11-undecylate	65.3	16.5	18.6 C ₁₁ H ₂₀ O ₂
9,10-undecynolic acid (found)	61.4	14.4	24.3 C ₁₁ H ₂₀ O ₂
Calcd. for a mercuric diacetoxymercuri-keto-undecylate	61.4	14.5	24.5 C ₁₁ H ₂₀ O ₂
Ethyl dehydro-undecylenate, found	59.9	17.3	22.6 C ₁₃ H ₂₄ O ₂
Calcd. for ethyl triacetoxy-mercuri-2-keto-11-undecylate	60.0	17.6	22.7 C ₁₃ H ₂₄ O ₂
Ethyl 9,10-undecynolate, found	53.8	15.6	30.4 C ₁₃ H ₂₄ O ₂
Calcd. for an ethyl diacetoxy-mercuri-keto-undecylate	53.8	15.8	30.6 C ₁₃ H ₂₄ O ₂

to bring the flask to constant weight. The analyses of the ketonic compounds thus obtained are described later.

Preparation of the Ketonic Compounds without Isolation of Mercuric Compounds.—Almost quantitative yields of the ketonic compounds were obtained from the acetylenic acids and esters by treating with the amounts of mercuric oxide and acetic acid stated and then adding concd. hydrochloric acid to the whole of the solution and pouring into water. The solid separating was filtered off and then treated with ether to separate from mercurous acetate. The filtrate was extracted with ether, the ether distilled and acetic acid blown off at the bellows or distilled under diminished pressure. The products were, if solid, recrystallized from petroleum ether. Esters were extracted with ether after being poured into water and fractionated under diminished pressure.

Properties of 2-Keto-11-undecylic Acid.—The acid crystallized in fine tufts of colorless needles or in small glistening leaflets. No regularity has been observed in the occurrence of these two forms. The crystals melt sharply at 59.5° . They are moderately soluble in hot petroleum ether (b. p. $60-80^{\circ}$) and practically insoluble in cold. They are slightly soluble in boiling water and almost insoluble in cold. The solubility in other organic solvents is considerable.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.95; H, 10.00; equiv. wt., 200.16. Found: C, 65.89; H, 10.17; equiv. wt. (titration with standard alkali), 200.

The ethyl ester boils at $169-170^{\circ}$ (corr.) (12 mm.). It gives no indication of enolization. The semicarbazone, prepared by adding a solution of semicarbazide hydrochloride with slightly more than the equivalent amount of sodium acetate to a solution of the acid in dil. alcohol, melts at 136.5° (corr.) after recrystallization from alcohol.

Anal. Calcd. for $C_{13}H_{22}O_3N_2$: C, 55.99; H, 9.01; N, 16.34. Found: C, 55.91; H, 9.08; N, 16.27.

The oxime prepared in the usual manner melts at $68-69^{\circ}$. When warmed on the water-bath for an hour with five times its weight of concd. sulfuric acid and then poured into water it is converted into a mixture of the isomeric acids $CH_3NHCO(CH_2)_8COOH$ and $CH_3CONH(CH_2)_8COOH$, melting after recrystallization from alcohol between 65 and 72° .

Anal. Calcd. for $C_{11}H_{21}O_2N$: C, 61.34; H, 9.84; N, 6.51. Found: C, 61.30; H, 9.91; N, 6.38.

Anal. (oxime). Found: C, 61.26; H, 9.90; N, 6.47.

Ten g. of the mixed acids after the Beckmann change was heated with 30 cc. of hydrochloric acid solution (saturated at room temperature) for five hours at $180-190^{\circ}$ in a sealed tube. The contents were washed into a flask and steam distilled for 30 minutes. The contents of the flask were made alkaline and again steam-distilled for 30 minutes. The residue in the flask was concentrated to 100 cc. and acidified. Crystals separated and these were recrystallized from water. They melted at 134° and were recognized as sebacic acid by the mixed melting point of 134° with sebacic acid derived from the oxidation of dehydro-undecylenic acid. The yield of sebacic acid was 4 g.

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The authors are indebted to the Government Grant Committee of the

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The oxime was found to give an almost quantitative yield of 2-keto-11-undecylic acid on hydrolysis with dil. sulfuric acid.

The authors are indebted to the Government Grant Committee of the

Royal Society for a grant which defrayed part of the cost of the investigation.⁴

Summary

1. Crystalline compounds containing mercury are produced by the action of mercuric acetate in acetic acid solution upon dehydroundecylenic and 9-10 undecinic acids and upon their ethyl esters.

2. The mercury compounds yield, after treatment with hydrochloric acid, saturated ketonic acids or esters free from mercury. Hydration at the triple bond has thus been effected.

3. Hydration in the case of dehydroundecylenic acid takes place in one direction, but in the case of 9-10 undecinic acid in the two theoretically possible directions with formation of two isomeric ketonic acids. The ethyl esters behave in the same manner.

LONDON, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE,
UNIVERSITY OF LONDON]

UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS

II. THE REACTION BETWEEN MERCURIC ACETATE AND SOME ACETYLENIC ACIDS AND ESTERS

BY WILLIAM WHALLEY MYDDLETON, RUDOLPH G. BERCHEM AND ARTHUR W. BARRETT

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Two of the present authors have described the isolation of mercury compounds resulting from the action of mercuric acetate upon dehydroundecylenic acid and 9,10-undecinic acid.¹

These examples include one case in which the acetylenic bond is at the end of a carbon chain and one in which it occurs along the chain and without any associated hydrogen atom.

In the present investigation we have varied the type of acetylenic acid by studying the action of mercuric acetate upon (a) stearic acid, (b) ricinolic acid, (c) behenic acid, (d) methyl behenolate, (e) γ -butinene- α,α -dicarboxylic acid, (f) γ -butinene- α -carboxylic acid.

Preparation of the Acetylenic Acids

A preliminary investigation of the methods of preparation of stearic, ricinolic and behenic acids was considered desirable. They are obtained by brominating oleic, ricinoleic and erucic acids, respectively, the

⁴ Since this work was completed the authors have noted that Chuit, Boelsing, Hausser and Malet [*Helv. chim. Acta*, 9, 1074 (1926)] describe the preparation of 2-keto-11-undecydic acid by oxidation of undecane-2,11-diol. The melting point recorded by these investigators is 58.5-59.5°.

¹ Myddleton and Barrett, *THIS JOURNAL*, 49, 2258 (1927).

dibromo acids so formed being then heated with concd. alcoholic or aqueous potassium hydroxide at temperatures between 150 and 180°. The purification of oleic acid and ricinoleic acid is extremely tedious, but it was found unnecessary to arrive at extreme purity in order to obtain the pure acetylenic acids.

(a) **Stearolic Acid.**—The oleic acid for this preparation was derived from olive oil. Analysis had shown that the mixed fatty acids from this oil contain 14.6% of palmitic acid, 10% of linoleic acid and 75.4% of oleic acid.²

It was found sufficient to remove all but traces of palmitic acid by converting the total mixed acids into lead salts and extracting the lead oleate and linoleate with ice-cold ether. The acids regenerated by dil. sulfuric acid were converted into the lithium salts by boiling with an excess of lithium carbonate suspended in water. The lithium salts were recrystallized once from dil. alcohol. Oleic acid of sufficient purity was obtained from the less soluble fraction.

(b) **Ricinolic Acid.**—Castor oil used for the preparation of ricinoleic acid was found to contain 8% of stearic acid, 1% of dihydroxy-stearic acid, 7% of linolenic acid and 84% of ricinoleic acid. In view of this analysis the preparation of ricinolic acid employed by Mangold³ by direct bromination of castor oil followed by treatment of the bromo-glycerides with alkalis was considered unsound.

Stearic acid, therefore, was separated, together with the dihydroxy acid, through the insolubility of their lead salts in dry ether. Ricinoleic and linolenic acids were regenerated from the soluble lead salts and were either converted into lithium salts and recrystallized or into methyl esters and fractionally distilled. The less soluble lithium salt and the methyl ester fraction boiling at 225–227° (10 mm.) gave a sufficiently pure ricinoleic acid.

(c) **Behenolic Acid.**—Rape oil gave a mixture of fatty acids containing 98.8% of erucic acid and traces of lignoceric and arachidic acids. In this case it was found sufficient to brominate the whole of the mixed acids after hydrolysis or to brominate the oil without prior treatment.

(d) and (e) **γ -Butinene-carboxylic Acids.**— γ -Butinene- α,α -dicarboxylic acid and γ -butinene- α -carboxylic acid were prepared in a pure condition by the method described by Perkin and Simonsen.⁴

Action of Mercuric Acetate

The acetylenic compounds were dissolved in glacial acetic acid and warmed on the water-bath with a solution of mercuric oxide in the same

² Myddleton and Barry, "Fats, Natural and Synthetic," Benn, London, 1924, p. 107.

³ Mangold, *Monatsh.*, 15, 307 (1894).

⁴ Perkin and Simonsen, *J. Chem. Soc.*, 91, 821 (1907).

solvent. Reaction proceeded at temperatures between 70 and 100° with deposition of small amounts of mercurous acetate.

The mercury compounds were isolated by cooling the filtered solution and diluting with water. The butinene derivatives were exceptional in yielding relatively large amounts of mercurous acetate and a further product which proved to be a mixture of mercurous and mercuric salts of indefinite composition and from which no ketonic acid could be obtained. The acetylenic acids of higher molecular weight gave mercuric salts of diacetoxymercuri-ketonic acids in the form of microcrystalline needles. These salts were recrystallized from dil. acetic acid. They were found to be decomposed by hydrogen sulfide and hydrochloric acid with formation of ketonic acids.

Methyl behenolate gave the ester of a diacetoxymercuri-ketobehenic acid and this, after being shaken with cold dil. hydrochloric acid, gave a methyl ketobehenate.

In the preparation of ketonic acids it was found unnecessary to isolate the mercury compound. The whole of the acetic acid solution was treated with an excess of concd. hydrochloric acid and the mixture poured into water. The ketonic acid separated in good yield.

Analysis of the Mercuric Compounds

The method employed in the analysis of the mercury compounds is described in detail in the first paper.¹ The results obtained were as follows.

TABLE I
ANALYSES

Acetylenic compound	Mercury compound		
	Hg, %	CH ₃ COO, %	Ketonic acid or ester, %
Stearolic acid	54.77	12.68	32.3 C ₁₈ H ₃₄ O ₃
Calcd. for a mercuric diacetoxymercuri-ketostearate	54.81	12.90	32.6 C ₁₈ H ₃₄ O ₃
Ricinolic acid	53.81	12.6	33.3 C ₁₈ H ₃₄ O ₄
Calcd. for a mercuric diacetoxymercuri-hydroxyketostearate	53.87	12.69	33.7 C ₁₈ H ₃₄ O ₄
Behenolic acid	51.58	11.89	35.9 C ₂₂ H ₄₂ O ₃
Required for a mercuric diacetoxymercuri-ketobehenate	51.65	12.16	36.5 C ₂₂ H ₄₂ O ₃
Methyl behenolate	45.21	13.27	41.3 C ₂₂ H ₄₄ O ₃ CH ₃
Required for a methyl diacetoxymercuri-ketobehenate	45.30	13.33	41.59 C ₂₂ H ₄₄ O ₃ CH ₃

The Ketonic Acids Derived from the Mercury Compounds

Baruch,⁵ Goldsobel⁶ and Holt⁷ have investigated the action of concd.

⁵ Baruch, *Ber.*, 27, 172 (1894).

⁶ Goldsobel, *Ber.*, 27, 3121 (1894).

⁷ Holt, *Ber.*, 25, 962 (1892).

sulfuric acid upon stearolic, ricinolic and behenolic acids and have described the isolation of ketonic acids as products of the reaction. The constitution of the ketonic acid was in each case established by forming the oxime and effecting scission through the Beckmann transformation. Stearolic acid gave 10-ketostearic acid, ricinolic acid gave 10-keto-12-hydroxystearic acid and behenolic acid gave 14-ketobehenic acid.

We have prepared the ketonic acids by this method as well as by intermediate formation of acetoxymercuri compounds and find that the products are identical. The melting points of the ketonic acids and the parent acetylenic acids are given in Table II.

TABLE II
MELTING POINTS OF KETONIC ACIDS

Acetylenic acid	M. p., °C.	Ketonic acid, m. p., °C.	Method of formation or observer
Stearolic acid	48.0	75-76	Mercury compd.
	48.0	76	Baruch
Ricinolic acid	53.5	84-85	Mercury compd.
	53.0	84-85	Goldsobel
	51.0	78-80	Mangold
Behenolic acid	57.5	83-84	Mercury compd.
	57.5	83	Holt and Baruch

In view of the observation of Myddleton and Barrett¹ that 9,10-undecynolic acid yields a mixture of two ketonic acids, and considering also the suggestion of Robinson and Robinson² that hydration of a triple bond may take place in each of the two possible directions, we submitted the ketonic acids prepared from the mercury compounds to the process of purification described by Robinson and Robinson. The melting points of the purified acids were as follows: 10-ketostearic acid, 76°; 10-keto-12-hydroxystearic acid, 85.6°; 14-ketobehenic acid, 84.5°.

The last two observers we have mentioned found that by treating stearolic acid with concd. sulfuric acid and then pouring into water, according to the method of Baruch, they obtained a mixture of ketonic acids from which, after a troublesome and wasteful process of purification, it was possible to isolate a small amount of a ketostearic acid melting at 83°. The high-melting acid was obtained in better yield by dissolving stearolic acid in concd. sulfuric acid and exposing the solution to moist air in an open vessel. They assume that the acid they have isolated is 10-ketostearic acid because it is indistinguishable from the product of a synthesis which seems capable of yielding only 10-ketostearic acid. We were not able to raise the melting point of our ketostearic acid above 76° by careful purification. This fact, together with the observation of Behrend³ that a ketostearic acid whose oxime yields scission products indicative of

¹ Robinson and Robinson, *J. Chem. Soc.*, 127, 176 (1925); 128, 2204 (1926).

³ Behrend, *Ber.*, 29, 806 (1896).

the constitution 9-ketostearic acid melts at 83° , suggests the advisability of studying the oximes of the acids described by Robinson and Robinson. They have themselves suggested that 9-ketostearic acid is one of the products of hydration of stearolic acid.

According to the constitutions assigned to the ketonic acids under discussion by Baruch, Goldsobel and Holt the keto group occurs at carbon atoms of even number, counting the carboxyl carbon atom as one. The position of the acetylenic bond before hydration is thus fixed to two possible positions, either immediately preceding or following the keto group.

In the case of stearolic, ricinolic and behenolic acids we have found it impossible to isolate from each more than one ketonic acid after hydration but it is possible that very small amounts of a second may be formed. Myddleton and Barrett have found evidence of hydration in two directions in the case of 9,10-undecynolic acid. In such a case the constitution of the two ketonic acids would afford conclusive evidence of the position of the triple bond in the parent acid, but in this instance simpler and equally convincing evidence is found in the fact that dehydro-undecylenic acid which has the triple bond in the ultimate position yields the same ketonic acid.

It is in most cases impossible to determine the position of the original triple bond by reference to the constitution of one ketonic acid derived from the acetylenic compound. Account must necessarily be taken of the nature of the dibasic acid produced by oxidation of the acetylenic acid with such reagents as nitric acid and alkaline potassium permanganate, although this is decidedly unsatisfactory because the dibasic acid is usually formed in small amount.

It is probably safer to derive supporting evidence from the nature of the scission products of the ozonides of the ethylenic acid which may readily be prepared by reducing the acetylenic compound with zinc in the presence of titanous chloride.

We propose to continue the investigation of the mercury compounds we have described to ascertain the position of the acetoxymercuri groups. If this is achieved another method of deciding the position of triple bonds in acetylenic acids and esters will be available.

Experimental Part

Bromination of Oleic, Ricinoleic and Erucic Acids.—The procedure was the same in the three cases. The acid was dissolved in a small volume of glacial acetic acid and a solution of bromine in acetic acid was stirred in at a temperature of 5° until excess bromine was indicated by starch-iodide paper after an hour's interval. The solution was allowed to stand overnight in the ice chest, after which it was poured into a large volume of water. The oily layer was washed with cold water and then with warm

water and finally with a dilute solution of sodium thiosulfate. After a final washing, the product was dried over calcium chloride. In the case of erucic acid the drying was omitted and the semi-solid product recrystallized from alcohol. Rape oil brominated in a similar manner gave a viscous oil which was dried over calcium chloride.

The characteristics of the products were as follows: oleic acid and ricinoleic acid gave a viscous oil; erucic acid gave a solid which after recrystallization from alcohol melted at 42–43°.

Conversion of Dibromo Acids into Acetylenic Acids.—Each dibromo acid was heated to gentle boiling in a solution of twice its weight of potassium hydroxide in eight times its weight of alcohol. For the treatment of brominated rape oil twice the proportion of alkali and alcohol was used. The reaction was complete after seven or eight hours' refluxing in a capacious flask heated in an oil-bath.

The bulk of the alcohol was then slowly distilled, the residue dissolved in water and the solution acidified with hydrochloric acid. The oily layer which separated was induced to crystallize by skimming off and stirring with fresh water.

Action of Mercuric Acetate upon the Acetylenic Acids.—The reaction was carried out as already described with the following amounts of reactants and solvent: acetylenic acid, 1 mole; mercuric oxide, 2.6 moles dissolved in five times the total weight of acetic acid. Methyl behenolate required the following proportions: ester, 1 mole; mercuric oxide, 2.1 moles dissolved in five times the total weight of acetic acid.

The products were recrystallized from 75 to 50% acetic acid.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant which defrayed part of the cost of the investigation.

Summary

1. Mercuric acetate reacts with stearolic, ricinolic and behenolic acids in acetic acid solution to form crystalline mercuric salts of diacetoxymercuri-ketonic acid.

2. The mercury compounds yield saturated ketonic acids after treatment with hydrochloric acids.

3. When mercuric acetate reacts with γ -butinene- α,α -dicarboxylic acid and with γ -butinene- α -carboxylic acid a mixture of mercuric and mercurous salts of indefinite composition results. No ketonic acid has been isolated after treating the mercury compounds with hydrochloric acid.

4. Methyl behenolate gives rise to a crystalline ester of a diacetoxymercuri keto-behenic acid. Hydrochloric acid liberates from this methyl 14-ketobehenate.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ARYLSULFURCHLORIDES AND ARYLSULFURANILIDES

BY E. GEBAUER-FÜLNEGG¹

RECEIVED MAY 17, 1927

PUBLISHED SEPTEMBER 2, 1927

There are two types of arylsulfurchlorides described in the literature: first, substances containing a nitro group in position ortho to the sulfur-chloride radical² and, second, compounds which have no nitro group in the molecule, the ortho and para positions being free or substituted.³

Both types of substances are colored intensely orange-red. But while the arylsulfurchlorides of the first class give highly-colored derivatives, we find the derivatives of the second class (with no substitution of a nitro group) to be colorless. Zincke, who first prepared and studied these substances, has already stated these facts.³ He concluded that the color of the mother substances is due to the sulfur-chlorine linkage, while the color of the derivatives is caused by the nitro group.

Lecher, who prepared the phenylsulfurchloride,⁴ attributes the color of this compound to the loose sulfur-chlorine bond, calling it a new chromophore. He also shows the analogy to SCl_2 .⁵ Neither explanation is entirely satisfactory, as they do not explain the different appearance of the derivatives of the two types of arylsulfurchlorides from a unifying point of view. That the sulfur-chlorine linkage is undoubtedly a loose one is readily apparent from the high reactivity of the compounds and from the investigations of Lecher. Another interesting behavior may be noted. If they are treated in indifferent solvents with hydriodic acid, iodine is immediately liberated; but if they are shaken with silver nitrate or silver carbonate, silver chloride is precipitated even with careful exclusion of moisture. Thus, the arylsulfurchlorides seem to exhibit the properties of chlorine in hydrochloric acid as well as chlorine in sodium hypochlorite. From an electronic conception this dual behavior indicates that these sulfurchlorides, when submitted to the action of different classes of reagents, react as if electromers were present. Experiments on this matter have been carried out with the 4-chloro-2-nitrophenylsulfurchloride.

That this peculiar behavior of the chlorine atom as such in these compounds is not responsible for the color of the arylsulfurchlorides, can be shown by comparison with the analogous aliphatic chloro-amines. Here, too, we find that addition of hydriodic acid is followed by liberation of

¹ International Research Fellow.

² Zincke, *Ann.*, **416**, 86 (1918).

³ Zincke and Eismayer, *Ber.*, **51**, 755 (1918).

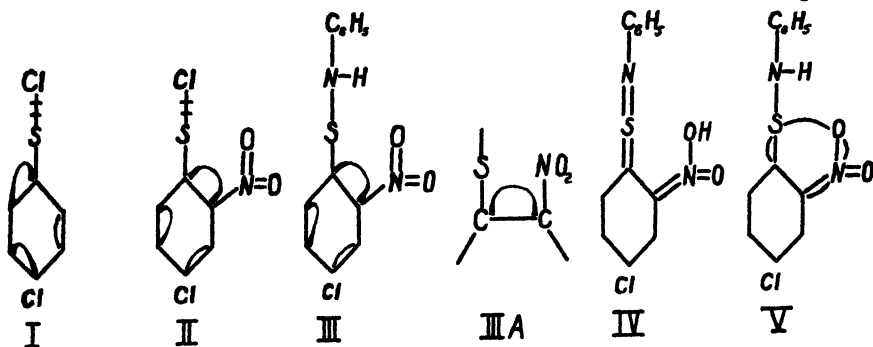
⁴ Lecher and Holschneider, *Ber.*, **57**, 755 (1924).

⁵ In this case the suggestion that the behavior of the sulfur-chlorine bonds is the direct cause for the development of color is very probable as no further alteration of the molecule can occur.

iodine but, on the other hand, reactions occur with potassium cyanide.⁶ The chloro-amines are not appreciably colored. Furthermore, this loose sulfur-chlorine linkage itself does not seem to be the essential chromophore, as Lecher has suggested. It seems, rather, to cause an alteration⁷ of the benzoid structure of the molecule and, as a consequence of a shifting of the valences, a quinoid state in the benzene ring is approached. This assumption does not imply that a fixed quinoid structure in the customary sense of the word results from these valence changes.⁸

In order to make this assumption clear, it will be explained and discussed on the example of a definite nitro-substituted arylsulfurchloride and an anilide.

The 4-chloro-2-nitrophenylsulfurchloride (II) is unsaturated. We accordingly find, as already mentioned, a tendency for a quinoid structure initiated by the loose sulfur-chlorine bond. This unsaturated state of the molecule remains the same when the anilide (derivative) is formed, because of the unsaturation of the nitro group itself. Therefore, the approached "quinoid" structure of the derivative of type (III) is possible. An aci form (IV), too, is conceivable. In the formulas the attempt has



been made to indicate this unsaturation of the molecule by means of curved lines, which represent primary valences not yet shifted to the quinoid end-stage. It is difficult to express this conception with the usual symbols for quinones since we associate with them only an end-stage of unsaturation in the molecule.

To decide whether the actual structure of the 4-chloro-2-nitrophenyl-sulfuranilide is that expressed in formula (III) or the aci form (IV), the corresponding methylanilide was prepared. In case that the latter (or any ring formation, where the anilido-nitrogen atom participates) should

⁶ Berg, *Ann. chim. phys.*, [7] 3, 338, 350 (1897).

⁷ For a similar conception, to a certain extent, see Georgievics, "Die Beziehungen zwischen Farbe und Konstitution," Schulthess and Co., Zurich, 1921, pp. 14-15.

⁸ Difficulties encountered in avoiding the formation of higher chlorinated products by some arylsulfurchlorides, Ref. 3, for other references see Ref. 4, seem to indicate the expected higher reactivity of such "quinoid" substances.

prove correct, a distinctly less colored derivative would have been expected but, as a matter of fact, a highly-colored orange solution was obtained, indicating that equilibration of the valence forces occurs in the grouping as expressed in formulas (III) and (IIIa). However, from the point of view of the theory of H. Kaufmann⁹ a ring formation through residual valences as indicated in formula (V), too, could explain the color phenomena encountered; but the assumption of the approached quinoid state seems to simplify the matter, involving no conception of a "Valenzersplitterung" and besides representing better the impression of valence force fields.

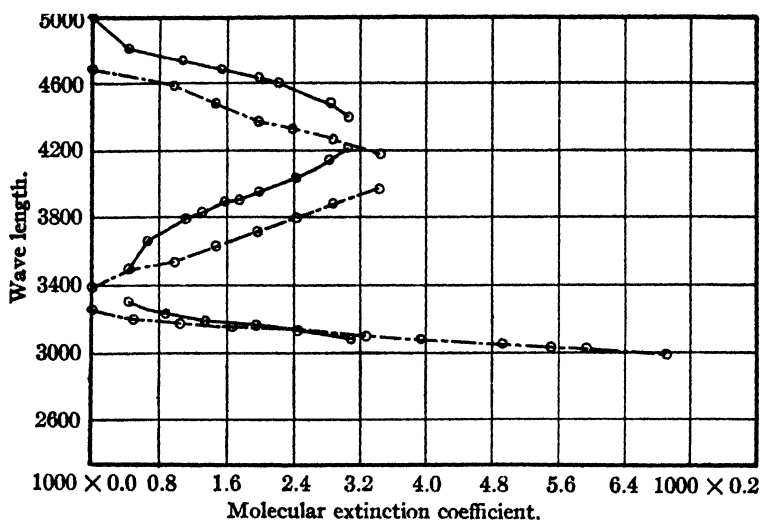


Fig. 1.— — = 4-chloro-2-nitrophenylsulfurchloride, 0.000449 *M*; - - - = 4-chloro-2-nitrophenylsulfuranilide, 0.0002018 *M*, in CHCl_3 .

In the molecule of the arylsulfurchlorides not substituted with a nitro group we find the same loose sulfur-chlorine bond, causing a similar shifting of the valence forces in the whole molecule. But by replacing it by the stronger sulfur-nitrogen linkage, shifting back to the benzoid structure occurs, as there is no possibility of maintaining the initial state, as a consequence of the lack of another unsaturated group. From this point of view, the explanation of the fact of the color in the case of the nitro-substituted arylsulfurchlorides and their derivatives has been shown to be as easy as the explanation of the fact that the derivatives of the also highly-colored sulfurchlorides, not substituted with a nitro group, are colorless.

To verify this assumption, Mr. Palmateer of Chicago University was kind enough to take pictures of the absorption spectra of 1, (a) 4-chloro-2-nitrophenylsulfurchloride and (b) 4-chloro-2-nitrophenylsulfuranilide; 2, (c) 4-chlorobenzenesulfurchloride, (d) 2,5-dichlorobenzenesulfurchloride,

⁹ Kaufmann, "Die Auxochrome," Ahrens Vorträge, 1908, 12, 1.

(e) 2,5-dichlorobenzenesulfuranilide. The pictures show that the colored substances (a)-(d) appear to have the same structure, and (a) and (b) check almost exactly. No change in the degree of unsaturation occurred through the formation of the anilide. From that it follows that the cause for the color from (a) and (b) is the same, not as Zincke suggested a different one. That the S-Cl bond as such is not the chromophore can be deduced from the same fact. If this were the case we should expect an altered curve for (b), as the supposed chromophore has been changed chemically.

Furthermore, the similarity of (a) and (c) shows that the nitro group as such has no essential part in the development of the color, but only augments the rise of the curves.

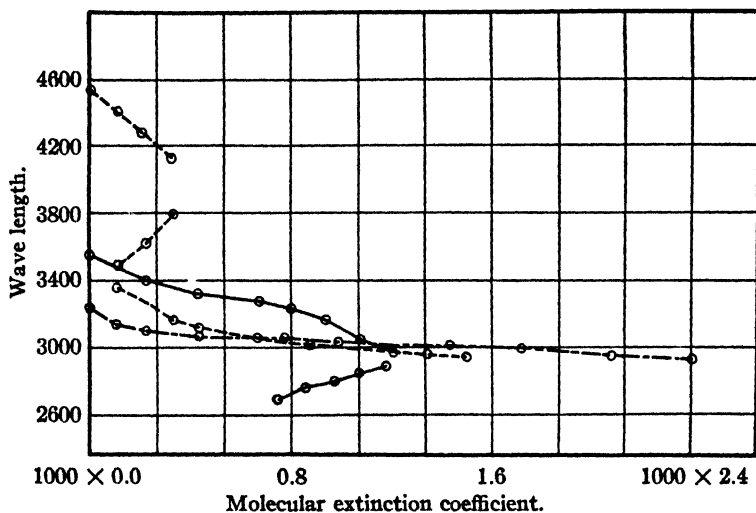


Fig. 2.— $M/1000$ ---- = 4-chlorobenzenesulfurchloride; $M/1000$ — = 2,5-dichlorobenzenesulfurchloride; $M/1000$ - - - = 2,5-dichlorobenzenesulfuranilide in CHCl_3 .

Finally, we see in (e) a new form of the absorption spectrum, indicating an entire change in the structure.

The substances (c) and (d) which were prepared show in their chemical and physical properties a distinct analogy to the phenylsulfurchloride of Lecher, and they have been prepared in the same way. In addition, an anilide of the 4-chloro-2-nitrophenylsulfurchloride was prepared with amino-azobenzene, which is highly red in color. The 4-chloro-2-nitrophenylsulfur radical produced in this case, as expected, a positive color change. It might be possible to utilize this observation in dyestuff chemistry. I hope to present in the future other cases in which an approached quinoid state of organic substances will explain color phenomena.

Experimental Part

The 2,5-dichlorobenzenesulfurchloride was prepared by dropping a solution of 5 g. of well-dried 2,5-dichlorothiophenol into 150 cc. of dry, ice-cold carbon tetrachloride through which was passed a slow current of chlorine. During the reaction the solution, which became yellow, was well stirred. After evaporating the carbon tetrachloride in vacuo the product was obtained by fractionation in a high vacuum. The substance which boiled constantly under 3 mm. at 92° analyzed well for a 2,5-dichlorobenzenesulfurchloride.

Anal. Subs., 0.0971, 0.1511: AgCl, 0.1970, 0.3060; BaSO₄, 0.1080, 0.1667. Calcd. for C₆H₃Cl₂S: Cl, 49.86, S, 15.03. Found: 50.19, 50.10, 15.28, 15.15.

The corresponding anilide was obtained by treating one molecule of the 2,5-dichlorobenzenesulfurchloride with two molecules of redistilled aniline in well-dried chloroform or carbon tetrachloride. After filtration from aniline hydrochloride and evaporation of the filtrate in a vacuum, the residue was crystallized from ligroin. White needles melting at 85° were obtained.

Anal. Subs., 0.1002: N, 4.6 cc. (763 mm., 22°); 0.1294 g., 5.9 cc. (765 mm., 20°). Calcd. for C₁₂H₇Cl₂SN: 5.19. Found: 5.33, 5.35.

The 4-chlorobenzenesulfurchloride was obtained in an analogous way to the 2,5-dichlorobenzenesulfurchloride. Its boiling point under 6 mm. pressure was 94°.

Anal. Subs., 0.1643, 0.1081: AgCl, 0.2650, 0.1740; BaSO₄, 0.2177, 0.1417. Calcd. for C₆H₄Cl₂S: Cl, 39.62; S, 17.92. Found: 39.90, 39.81, 18.20, 18.00.

If one molecule of 4-chloro-2-nitrobenzenesulfurchloride in ether solution is treated with an ethereal solution of amino-azobenzene, reaction occurs. After filtering off the amino-azobenzene hydrochloride which forms, red crystals are obtained by evaporation of the solution. On recrystallization from ether they melt at 188°. The values from the N combustion agree well with the calculated figures for an anilide of 4-chloro-2-nitrophenylsulfurchloride with amino-azobenzene.

Anal. Subs., 0.1424, 0.1167: N, 18.3 cc. (758 mm., 22°), 14.9 cc. (760 mm., 22°). Calcd. for C₁₈H₁₃N₄O₂ClS: N, 14.56. Found: 14.83, 14.77.

2,4-Diamino-azobenzene and 4-chloro-2-nitrobenzenesulfurchloride react apparently in the same way, yielding small brownish-red crystals.

To prepare the 4-chloro-2-nitrophenylsulfurmethylanilide, 2 moles of methylaniline were treated with 1 mole of 4-chloro-2-nitrophenylsulfurchloride in absolute ether solution. After filtration, the deeply-colored solution was evaporated. The resulting orange-red, sirupy mass could not be obtained in a crystalline form, but solidified after several days. No better results have been observed by the use of other solvents such as chloroform and redistilled methylaniline. Further attempts to obtain this product in a crystalline form will be made. The analysis of the solidified material showed the presence of the expected product.

Anal. Subs., 0.1329, 0.1537: N, 11.1 cc. (765 mm., 21°); 12.9 cc. (760 mm., 21°). Calcd. for C₁₄H₁₁N₂SClO₂: N, 9.51. Found: 9.76, 9.58.

The author wishes to express his appreciation to Professor Lauder W. Jones for his assistance in this investigation.

Summary

1. A modified conception of the quinoid theory of colored substances has been offered.

2. Color phenomena in the series of the arylsulfurchlorides and their derivatives have been discussed and explained from this point of view.

3. Absorption spectra of some arylsulfurchlorides and their anilides have been presented and discussed.

4. New arylsulfurchlorides and anilides have been prepared.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 40 FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY]

ACTION OF THE GRIGNARD REAGENT ON ALKYLBARBITURIC ACIDS

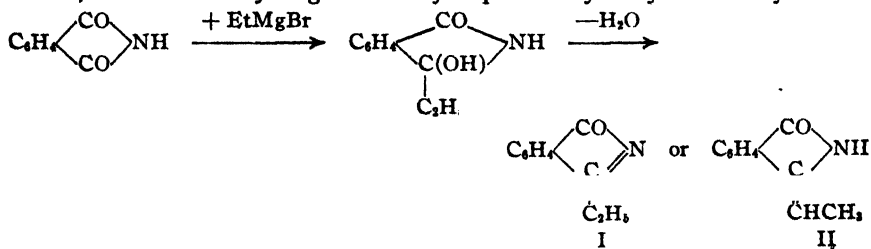
By ARTHUR W. DOX

RECEIVED MAY 18, 1927

PUBLISHED SEPTEMBER 2, 1927

The 5,5-dialkylbarbituric acids, a number of which have come into extensive use as sleep-producing drugs, all contain three carbonyl groups, one or more of which should be expected to react with the Grignard reagent. Although commonly termed "acids," because the unsubstituted parent substance has certain very pronounced acid properties, these derivatives possess more the character of imides. For example, their solubility in alkali is due to a replacement of imide hydrogen by metal. Although two such imide groups are present only one is thus replaceable.

According to Béis¹ the more familiar types of imides, such as phthalimide, react with the Grignard reagent, but here only one of the two carbonyls is affected. With Grignard reagent prepared from normal alkyl halides, Béis noted a dehydration of the initial reaction product. This is attributed to a splitting out of water between the hydroxyl on the nucleus and a hydrogen of the side chain. The product obtained from phthalimide and ethyl magnesium bromide would be, therefore, not an ethyl-*iso*-indolone (Formula I) but rather an ethylidene phthalimidine (Formula II). The phenyl group, on the other hand, cannot give up a hydrogen in this manner and dehydration does not occur, the product with phenyl magnesium bromide being a phenylhydroxy-*iso*-indolinone. However, Sachs and Ludwig² obtained from *N*-ethylphthalimide and ethyl magnesium bromide a product analogous to Béis' phenyl Grignard product. In other words, with imide hydrogen already replaced by alkyl the dehydration



¹ Béis, *Compt. rend.*, **138**, 987; **139**, 61 (1904).

² Sachs and Ludwig, *Ber.*, **37**, 388 (1904).

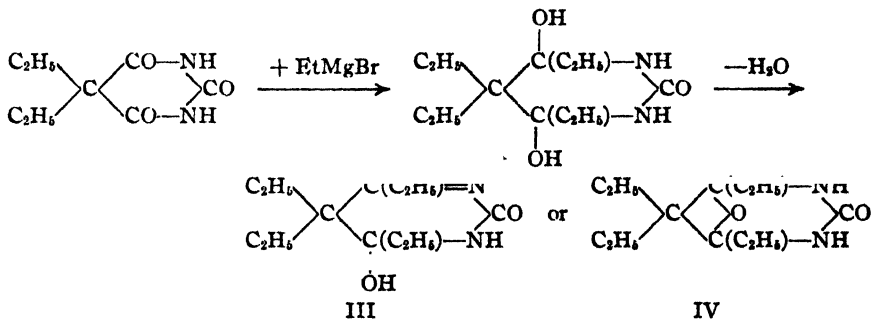
did not occur. The location of the double bond resulting from dehydration is still in question, leaving a choice between Formulas I and II.

With dialkylbarbituric acids and the Grignard reagent two carbonyls react, but in the dehydration which also occurs only one molecule of water is removed. Moreover, phenyl magnesium bromide gives the same type of product as do the alkyl magnesium bromides; and, further, a tetra-alkylbarbituric acid with no replaceable hydrogens gave a reaction between all three carbonyls and the Grignard reagent, but only one molecule of water was split out. The dehydration in the case of alkylbarbituric acid reaction products must, therefore, occur in a manner different from that represented in either Formula I or II.

Experimental

In all of the preparations described herein an excess of the Grignard reagent was used. To this was slowly added, with continuous stirring, an ethereal solution of the alkylbarbituric acid. Each drop gave momentarily a white precipitate, possibly a magnesium salt of the barbituric acid, which immediately dissolved again. After all had been added the mixture was refluxed for one and a half to two hours, and then treated in the usual way with dilute sulfuric acid. Products containing smaller alkyl groups had a tendency to crystallize out of the ether layer; those of higher molecular weight usually remained in solution and were obtained crystalline by evaporation of the solvent. Recrystallization from alcohol gave fine, slender needles. None of the products melted at 250° , and those with lower molecular weight sublimed without melting and apparently without decomposition.

Analysis of the product obtained from diethylbarbituric acid and ethyl magnesium bromide showed that two carbonyls had reacted and that one molecule of water had been split out. The calculated empirical formula is $C_{12}H_{22}O_2N_2$, which may be represented by either of two structures, III or IV.



For reasons to be discussed presently, Formula IV appears the more probable of the two. The substance will, therefore, be designated, pro-

visionally, endo ether of 4,6-dihydroxy-4,5,6-tetra-ethyl-2-ketohexahydropyrimidine. It is insoluble in water and benzene, moderately soluble in alcohol, but unlike diethylbarbituric acid it is insoluble in sodium hydroxide. Removal of any traces of unreacted dialkylbarbituric acid is easily effected by extraction with dilute alkali. The substance dissolves readily in concentrated sulfuric, hydrochloric and acetic acids, and is precipitated unchanged from these solutions by dilution with water.

Anal. Subs. 0.1446, 0.1577: CO_2 , 0.3394; H_2O , 0.1304; N_2 , 18.2 cc. (738 mm., 28°). Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2$: C, 63.72; H, 9.73; N, 12.39. Found: 64.01, 10.02, 12.29.

The substance is surprisingly resistant to hydrolysis. When the solution in concentrated hydrochloric acid is gently refluxed, the original substance separates out again as soon as the loss by evaporation diminishes the concentration of acid to the constant-boiling solution. After two hours' refluxing 94% of the original material was recovered unchanged. Six hours' heating in a sealed tube at 160–180° with ten parts of 25% sulfuric acid was insufficient to effect hydrolysis; 89% of the substance was recovered unchanged. Three hours' refluxing of 1 g. with 1 g. of potassium hydroxide in 50 cc. of alcohol likewise failed to effect hydrolysis, the recovery in this case being 89%. Hydrolysis was accomplished, however, by heating for seven hours at 150–160° in a sealed tube with ten parts of concentrated hydrochloric acid, and also by seven hours' heating in an oil-bath at 130–135° with 50% by volume sulfuric acid. The products obtained were ammonium chloride and sulfate, respectively, and a volatile oil with characteristic ketone odor. The oil, after purification by steam distillation, was soluble in water and reacted with hydroxylamine and with phenylhydrazine, forming liquid products which failed to crystallize in a freezing mixture. The initial products of hydrolysis should be a diketone of the formula $(\text{C}_2\text{H}_5)_2\text{C}(\text{COC}_2\text{H}_5)_2$ and urea. These probably undergo further hydrolysis to form diethylketone and ammonia.

In a similar manner other dialkylbarbituric acids reacted with various alkyl magnesium halides, giving products of much the same properties. In all cases the nitrogen content agreed with that calculated for products of the same type, that is, alkylation of two carbonyls and loss of one molecule of water.

DIALKYLBARBITURIC ACIDS + RMgBr

Barbituric acid	Grignard	Product	N	
			Calcd.	Found
Diethyl	Ethyl	$\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2$	12.39	12.29
Ethylphenyl	Ethyl	$\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_2$	10.22	9.98
Ethyl- <i>iso</i> -amyl	Ethyl	$\text{C}_{16}\text{H}_{28}\text{O}_2\text{N}_2$	10.11	10.16
Diethyl	Phenyl	$\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_2$	8.70	8.62
Diethyl	Propyl	$\text{C}_{14}\text{H}_{26}\text{O}_2\text{N}_2$	11.02	11.05
Diethyl	<i>n</i> -Butyl	$\text{C}_{18}\text{H}_{30}\text{O}_2\text{N}_2$	9.93	10.18
Diallyl	Ethyl	$\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}_2$	11.20	10.88
Diallyl	<i>iso</i> -Amyl	$\text{C}_{20}\text{H}_{34}\text{O}_2\text{N}_2$	8.38	8.37

The choice between Formulas III and IV could not be determined satisfactorily by hydrolysis whereby a ketone, probably diethylketone, was obtained. If the dehydration occurs between the tertiary alcohol grouping and the adjacent NH, it seems unlikely that only one molecule of water should be split out rather than two. On the other hand, the internal ether structure represented by Formula IV, which contains no double linkage, gives a symmetrical structure for which the observed stability and resistance to hydrolysis might be predicted.

If a similar dehydration takes place when a tetra-alkylbarbituric acid reacts with the Grignard reagent, the only manner in which it could occur would be by formation of an inner ether, since both nitrogens are substituted and no replaceable hydrogen is present. As will be shown directly, this is apparently what takes place.

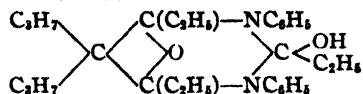
5,5-Dipropyl-1,3-diphenylbarbituric acid was prepared by dissolving molecular proportions of dipropylmalonic acid and carbanilide in anhydrous chloroform, adding two molecules of freshly distilled phosphorus oxychloride and heating the mixture in an oil-bath for four hours at 65–70°. The chloroform was then evaporated and the residue dissolved in water. Extraction with ether took up the condensation product, along with some dipropylmalonyl chloride, and precipitated out the unreacted carbanilide. Evaporation of the ether left a sirup which could not be crystallized. It was then purified by vacuum distillation. The portion distilling between 150 and 190° at 4 mm. solidified in the receiver, and after washing with petroleum ether and recrystallizing from benzene, it was obtained in white prisms melting at 104–105°. Unlike the di- and trialkylbarbituric acids, which contain replaceable hydrogen, this substance is insoluble in alkali. The yield was small (30%), owing probably to insufficient time of reaction.

Anal. Subs. 0.2254: N₂, 14.9 cc. (749 mm., 23°). Calcd. for C₂₂H₂₄O₂N₂: N, 7.69. Found: 7.35.

The above product was treated in the usual manner with ethyl magnesium bromide. No transient precipitate of a magnesium salt was formed during the reaction. The product after recrystallization from benzene consisted of white needles melting at 102°. A mixed melting point with the tetra-alkylbarbituric acid gave a depression of 8°.

Anal. Subs., 0.1979, 0.1992: CO₂, 0.5607; H₂O, 0.1664; N₂, 11.4 cc. (745 mm., 26°). Calcd. for C₂₈H₄₀O₂N₂: C, 77.06; H, 9.17; N, 6.42. Found: 77.27, 9.34, 6.35.

The empirical formula represents an endo ether of 1,3-diphenyl-2,4,6-triethyl-5,5-dipropyl-2,4,6-trihydroxyhexahydropyrimidine:



The analysis is not in agreement with values calculated for products that would result from the reaction of two carbonyl groups, with or without dehydration. Substitution of both NH groups in the barbituric acid evidently modifies the properties of the third carbonyl in such a way as to render it capable of reacting with the Grignard reagent.

Summary

The reaction between 5,5-dialkylbarbituric acids and the Grignard

reagent consists in the alkylation of two carbonyls and the loss of one molecule of water, probably with formation of an internal ether. With a tetra-alkylbarbituric acid the same reaction occurs, also an additional reaction of the third carbonyl.

DETROIT, MICHIGAN

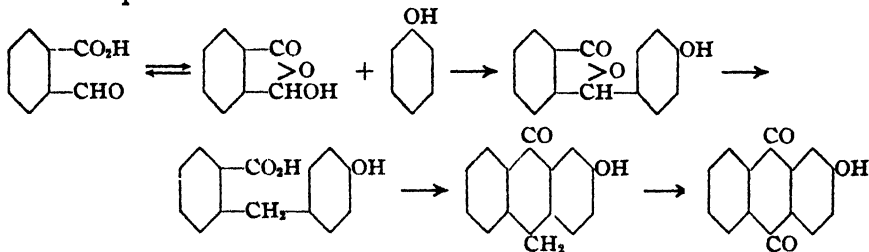
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]
**THE STRUCTURE OF THE CONDENSATION PRODUCTS OF
 ORTHO-PHTHALALDEHYDIC ACIDS WITH PHENOLS AND
 PHENOL ETHERS. VIII.¹**

BY M. M. BRUBAKER² WITH ROGER ADAMS

RECEIVED MAY 23, 1927

PUBLISHED SEPTEMBER 2, 1927

The preparation of substituted phthalides from *ortho*-phthalaldehydic acid by condensation with phenols was discovered by Bistrzycki.³ He found that the phthalides formed could be reduced to benzyl-benzoic acids and these in turn could be dehydrated and the anthrones oxidized to anthraquinones.



This procedure for preparing certain types of anthraquinones appeared, at first, not to be entirely general, since he was unable to reduce phthalides from opianic acid (2-carboxy-3,4-dimethoxybenzaldehyde) and phenols to the corresponding benzyl-benzoic acids. Jacobson and Adams,^{1d} however, found that under the proper conditions these latter phthalides could be reduced, and, although the benzyl-benzoic acids could not in all cases be obtained crystalline and pure, the products served well for the preparation of anthraquinones. In this Laboratory the method has already been applied to the synthesis of morindone,^{1e} rufiopin^{1g} and

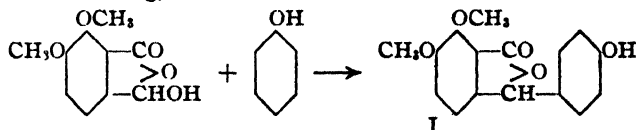
¹ For previous articles in this field see (a) Graves with Adams, *THIS JOURNAL*, **45**, 2439 (1923); (b) Gardner with Adams, *ibid.*, **45**, 2455 (1923); (c) Jacobson with Adams, *ibid.*, **46**, 1312 (1924); (d) **46**, 2788 (1924); (e) **47**, 283 (1925); (f) **47**, 2011 (1925); (g) Puntambeker with Adams, *ibid.*, **49**, 486 (1927).

² This communication is an abstract of a thesis submitted by M. M. Brubaker, Carr Fellow for 1926-1927, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ (a) Bistrzycki and Oehlert, *Ber.*, **27**, 2632 (1894); (b) Bistrzycki and Yssel de Schepper, *Ber.*, **31**, 2790 (1898); (c) Bistrzycki and Zen-Ruffinen, *Helv. Chim. Acta.*, **3**, 369 (1920); (d) Bistrzycki and Krauer, *ibid.*, **6**, 750 (1923).

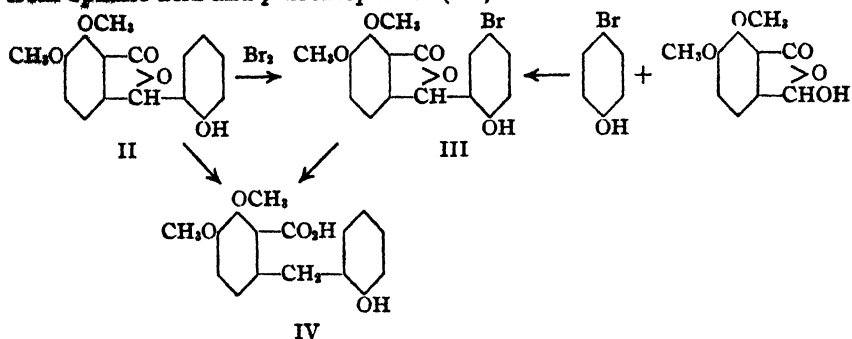
hydroxyanthrarufin. With a certainty of the reduction of the phthalides, the value of this procedure as a means of preparing hydroxyanthraquinones of various known structures depends upon a definite knowledge of the structure of the phthalide. Bistrzycki prepared beta-hydroxyanthraquinone by the series of reactions given above and thus demonstrated without question the structure of the intermediate phthalide; the condensation of the *o*-phthalaldehydic acid takes place *para* to the hydroxyl group of the phenol. He therefore assumed that when opianic acid was used in place of the unsubstituted *o*-phthalaldehydic acid, the condensation with phenol or substituted phenols always proceeded *para* to the hydroxyl. In a series of researches from this Laboratory,^{1e,1f,1g} the condensation was directed *ortho* to the hydroxyl group by starting with a *p*-halogenated phenol and the halogen was later removed during reduction to the benzyl-benzoic acid. From time to time in the course of these investigations, it appeared doubtful whether the condensation of opianic acid and phenols with both *ortho* and *para* positions unoccupied always went *para* to the hydroxyl group. Since the success of several problems depended upon a knowledge of this fact, a study was undertaken to determine the structure of the phthalides formed, in other words, the exact position assumed in the condensation of opianic acid with phenols and certain substituted phenols. This paper describes also the results of the condensation of opianic acid with phenol ethers, a continuation of the study of the condensation of *o*-phthalaldehydic acid with certain phenols, the condensation of bromo-opianic acid with phenol, and finally a new class of compounds, the *bis*-phthalidyl phenols or phenol ethers where two molecules of the *o*-phthalaldehydic acid condense with one of phenol or phenol ether.

Bistrzycki^{3a,b} condensed opianic acid with phenol and obtained what he considered to be the *para* condensation product (I), though it was obviously impure on account of the melting point reported (160–170° with previous softening).

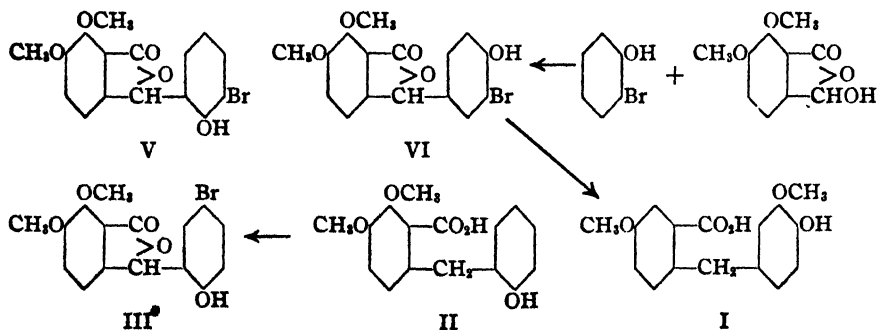


He was unable to reduce this compound to the corresponding benzyl-benzoic acid. A repetition of this reaction was carried out, and, by a different method of crystallization of the crude product, a pure compound was isolated which melted sharply about 20° higher than the m. p. reported by Bistrzycki. This product was shown without question to be that in which the condensation had taken place in the *ortho* position to the hydroxyl, (II), because on bromination the same monobromo compound (III) resulted as was formed by the condensation of opianic acid with *p*-bromo-

phenol. Moreover, upon reduction of the phthalide, the same benzylbenzoic acid was produced as that formed by the reduction of the phthalide from opianic acid and *p*-bromophenol (III).

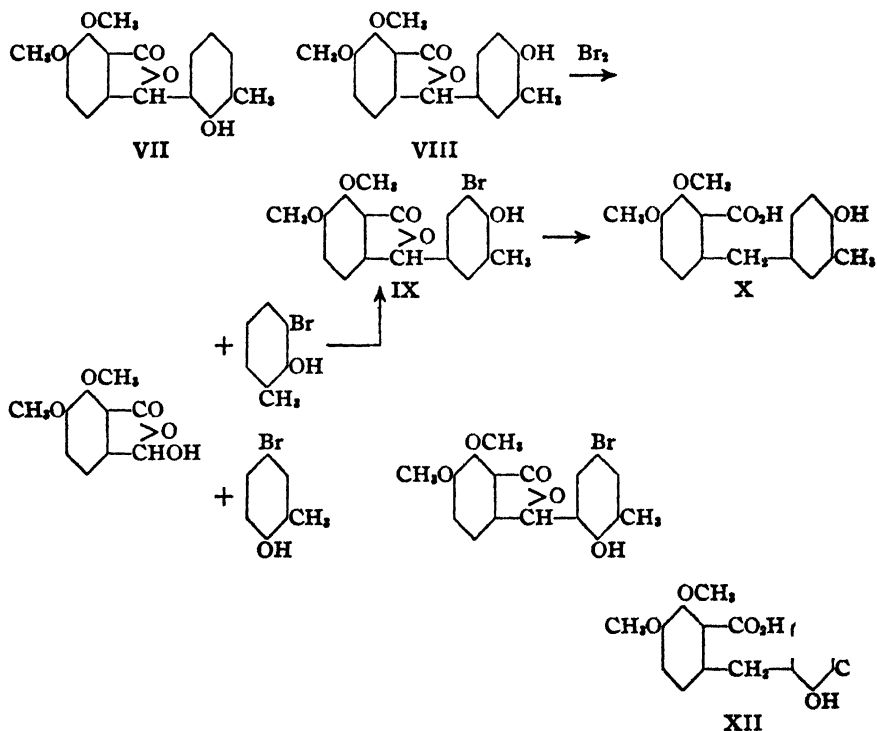


This demonstrated that the *ortho* condensation product (II) was formed to a large extent, contrary to what might be expected from Bistrzycki's work with *o*-phthalaldehydic acid. The presence of the *para* condensation product (I) was also demonstrated. It may be stated here that one of the outstanding characteristics of the condensation products from opianic acid and many of the phenols is the slow rate of crystallization. In some instances several days are required for complete crystallization even in the presence of a seed. This is particularly true if isomeric impurities are present and separations by crystallization are frequently rendered difficult, due to the formation of gums. It was discovered early in this work that the bromine derivatives could, in all cases, be crystallized much more readily, and mixtures of these bromo compounds could frequently be separated with comparative ease. Opianic acid was, therefore, condensed with phenol and the crude reaction product brominated in glacial acetic acid. A monobromo compound was readily isolated and purified. If, before bromination, both *ortho* and *para* condensation products were present, there are three possible structures for the brominated compound, (III), (V) and (VI), assuming that the bromine enters only the phenol nucleus.



The structure of the compound was shown to be that represented by (VI), namely, the monobromo derivative of the phthalide in which the opianic acid was condensed *para* (I) to the hydroxyl group of the phenol. This was demonstrated first by condensation of opianic acid with *o*-bromophenol, which gave the same substance (VI) in excellent yields, thus restricting the structure to (VI) or (V) and eliminating the possibility of bromination in the opianic acid ring. Upon reduction of the bromine compound (VI) a benzyl-benzoic acid resulted which was not identical with the benzyl-benzoic acid formed by reducing either the phthalide isolated from the reaction of opianic acid and phenol or the phthalide from opianic acid and *p*-bromophenol. Since the latter benzyl-benzoic acid must have the linkage *ortho* to the hydroxyl group, the new benzyl-benzoic acid must have the linkage *para*, and formula (V) is thus eliminated. The presence of both *ortho* and *para* compounds in the condensation of opianic acid with phenol is thus substantiated.

A similar plan of attack for the determination of the structure of the opianic acid and *o*-cresol compounds was followed. The probability is that a mixture of isomers, (VII) and (VIII), is also produced here.



Bistrzycki^{3c} isolated a substance which he was unable to reduce to the corresponding benzyl-benzoic acid. Jacobson and Adams repeated the

work and obtained apparently the same phthalide, but it melted several degrees higher than reported by Bistrzycki. A successful reduction of the compound to a benzyl-benzoic acid was carried out, though the latter was never obtained in a crystalline state. The phthalide, after isolation in essentially a pure state from the reaction mixture, was brominated and a monobromo product readily produced (IX). This was shown to be identical with the condensation product of opianic acid and *o*-bromo-*o*-cresol, demonstrating that the original reaction must have taken place *para* to the hydroxyl group. The reduction of this brominated product yielded a crystalline benzyl-benzoic acid (X). It is thus obvious that the benzyl-benzoic acids, like the phthalides, readily form gums unless the products are absolutely pure. Since the brominated phthalides are easily purified, it is desirable to use these substances as intermediates if a pure benzyl-benzoic acid is to be readily obtained. When opianic acid is condensed with *p*-bromo-*o*-cresol, the condensation undoubtedly goes *ortho* to the hydroxyl (XI). This was proved with certainty, because upon reduction a benzyl-benzoic acid results (XII) which is different from the one formed from the bromination of the phthalide from opianic acid and *o*-cresol. The isolation of the isomer was not attempted.

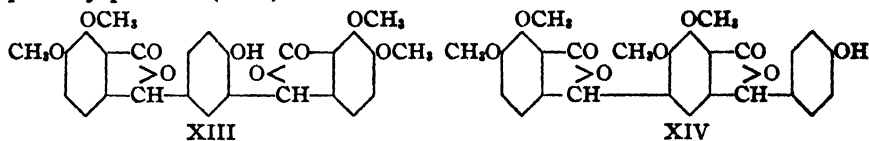
From the results with the phenol and *o*-cresol condensations, it is obvious that if the *ortho* and *para* positions to the hydroxyl of the phenol are open both isomeric forms are produced, and the pure compound isolated may be either, depending upon conditions used. An *ortho* condensation will take place if the *para* position to the hydroxyl group is occupied, and a *para* condensation if both the *ortho* positions to the hydroxyl are occupied. If only one position *ortho* to the hydroxyl is filled, probably the chief condensation will take place *para* to the hydroxyl. In the condensations with *o*-bromophenol and *o*-bromo-anisole, the yield of *para* condensation products was practically quantitative. With the *o*-cresol this was not true, and ordinarily it would be necessary to determine the structure of the product with certainty where the compound was to be used as an intermediate for structural work. The same conclusion in regard to orientation may be drawn about the phenol ethers which are described below.

Two products were isolated when opianic acid was condensed with *p*-bromo-*m*-cresol.¹⁸ Since three isomers are possible from the condensation of opianic acid and *m*-cresol, this reaction was not studied.

In many of the condensations of opianic acid with phenol and phenol derivatives, high-melting by-products were formed in small quantities. Analyses of these compounds revealed the fact that they were not simple phthalides, isomeric with the normal products, but *bis*-phthalidyl compounds formed from two molecules of opianic acid and one molecule of the phenol or phenol derivative. Experiments showed that the amount

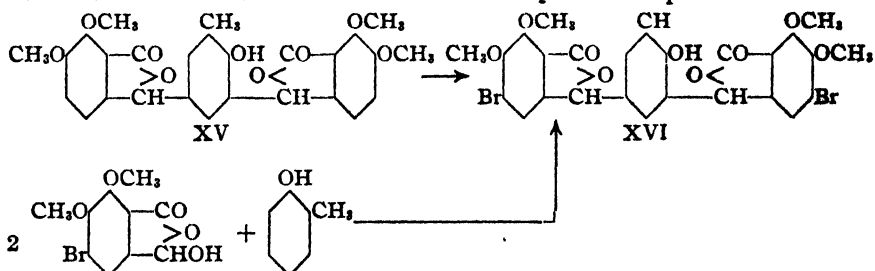
of by-product formed could be increased from small quantities to good yields by using two molecular proportions of opianic acid to one of the phenol or phenol derivative, and also by increasing the strength of the sulfuric acid used in condensation.

There are two possible structures for these compounds, one in which two molecules of opianic acid condense in the phenol ring, probably in the positions *ortho* and *para* to the hydroxyl (XIII), and the other in which an opianic acid molecule condenses in the opianic nucleus of the primary product (XIV).



Since the vacant positions in opianic acid are rather difficult to substitute, such a condensation as that represented by formula (XIV) would appear unlikely.

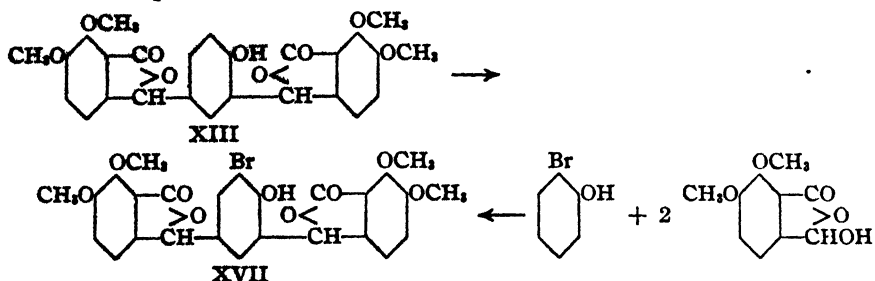
The structure of the *bis*-phthalidyl compound in the case of opianic acid and *o*-cresol was shown definitely to be (XV). If either the *ortho* or *para* position to the hydroxyl in the *o*-cresol nucleus is not occupied, bromination might be expected to take place readily in the cold, similar to the quantitative bromination in the cold of many analogous compounds, (see formulas VIII and IX). The *bis*-phthalidyl *o*-cresol derivative, however, could not be brominated at all in the cold. Upon heating with bromine in glacial acetic acid for two hours, two bromine atoms are introduced. The compound resulting from this bromination (XVI) was found to be identical with the *bis*-phthalidyl compound formed from bromo-opianic acid and *o*-cresol, showing that in the original bromination a bromine atom was introduced into each of the opianic acid nuclei.



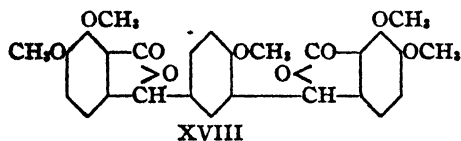
This establishes the fact beyond a doubt that the *o*-cresol ring is substituted in two positions and eliminates the possibility of formula (XIV).

The *bis*-phthalidyl compound from opianic acid and phenol has an *ortho* position to the hydroxyl in the phenol nucleus unfilled (XIII). Bromination might then be expected to take place in the cold with the entrance of a single bromine atom into the phenol nucleus. This actually

occurs and a compound (XVII) was produced, identical with the *bis*-phthalidyl compound obtained from the condensation of opianic acid and *o*-bromophenol.



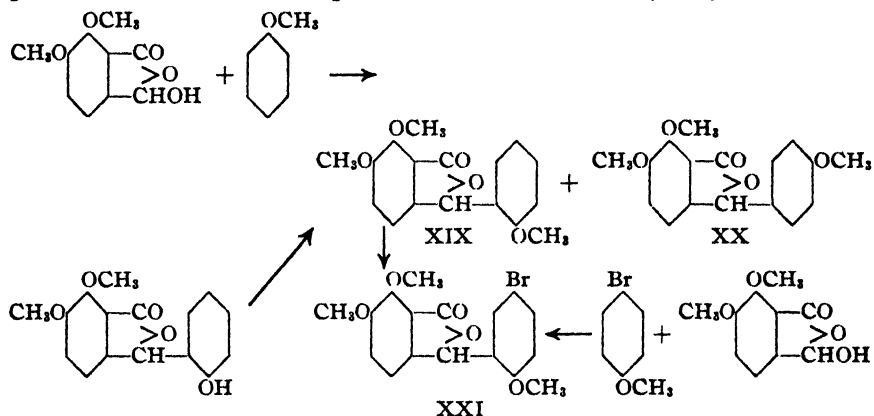
The above experiment also indicates that two opianic acid nuclei have condensed with phenol in the positions *ortho* and *para* to the hydroxyl, rather than in the two *ortho* positions. Methylation of the *bis*-phthalidyl compound from opianic acid and phenol gives a compound identical with the *bis*-phthalidyl derivative from opianic acid and anisole, so its structure may be represented by formula (XVIII).



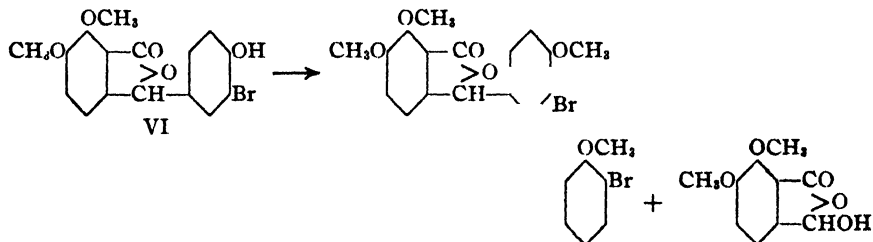
Early experiments by Bistrzycki^{3a} indicated that *o*-phthalaldehydic acid could not be condensed with phenol ethers, for no product was obtained from *o*-phthalaldehydic acid and phenetole. He was able later,^{3c} however, to condense opianic acid and *o*-phthalaldehydic acid, with both *o*-cresol methyl ether and veratrole. It has been shown in this investigation that the condensation of opianic acid and *o*-phthalaldehydic acid with phenol ethers is as general a reaction as that with phenols; *o*-phthalaldehydic acid has been condensed with anisole and *p*-bromo-anisole, and opianic acid has been condensed with anisole, *p*-bromo-anisole, *o*-bromo-anisole and *p*-bromo-*m*-cresol methyl ether.

It is very difficult to obtain a pure phthalide from opianic acid and anisole. Considerable *bis*-phthalidyl compound from the condensation of two molecules of opianic acid and one of anisole (XVIII) is formed, due probably to the fact that the anisole is not as soluble as the opianic acid in the 73% sulfuric acid used as a condensing agent, with the result that there is an excess of the opianic acid always present in solution. The gum from the condensation has been shown to contain both isomeric phthalides (XIX) and (XX). By very slow and tedious crystallization, small amounts of the *para* isomer (XX) may be isolated. That the compound was the *para* isomer was concluded from the fact that it was not identical with

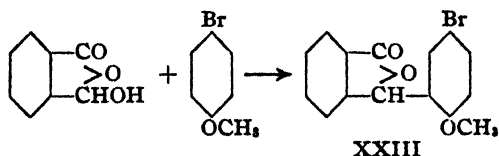
the *ortho* isomer prepared by the methylation of the *ortho* hydroxyl compound (II), the determination of the structure of which was described earlier in the paper. If the crude product is brominated directly, a bromo derivative (XXI) can be separated, identical with the condensation product of opianic acid and *p*-bromo-anisole, thus indicating that a portion of the condensation product is the *ortho* isomer (XIX).



In contrast to the mixture of isomers and the poor yield which is obtained in the condensation of opianic acid with anisole, a quantitative yield of a pure product is obtained with *o*-bromo-anisole, the structure of which has been shown to be (XXII), for it is identical with the compound obtained by methylation of the phthalide from opianic acid and *o*-bromophenol (VI) and the structure of the latter has already been established.

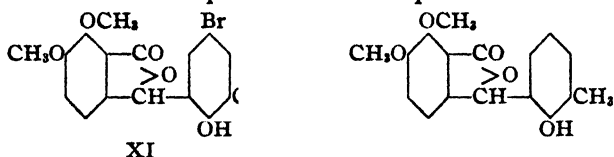


As in the condensation with phenol so with anisole, the simple *o*-phthalaldehydic acid gives more readily crystallizable products, and a fair yield of the *para* isomer with anisole may be isolated. *o*-Phthalaldehydic acid also condenses with *p*-bromo-anisole to give a product which has, undoubtedly, the structure (XXIII).



bis-Phthalidyl compounds from *o*-phthalaldehydic acid were not isolated as by-products in forming the phthalides, and an attempt has not yet been made to modify conditions so as to obtain them.

In determining the structure of the pure phthalides isolated from the condensations of opianic acid with phenol, anisole, *o*-cresol and *m*-cresol, an attempt was made to produce the pure *ortho* phthalides for comparison by catalytic reduction of the halogen from the halogenated phthalides formed by the condensation of opianic acid and *p*-bromophenols. Blocking the position *para* to the hydroxyl directs the condensation to the *ortho* position. Consequently, as, for example, in the case of the phthalide from opianic acid and *p*-bromo-*o*-cresol, if the removal of the halogen from this phthalide (XI) could be effected, a compound would result which would be the phthalide from opianic acid and *o*-cresol, provided the condensation had taken place in the *ortho* position.



Catalytic reduction with platinum-oxide platinum black was not satisfactory for this reaction because after the halogen was replaced by hydrogen in part of the material, further reduction took place in the product before all of the original bromine compound was reduced. This is due, in part at least, to the fact that the bromine compounds used are not very soluble in the alcohol employed as a solvent and have to be reduced in partial suspension. It was not possible in any instance to stop the reduction at the desired point. From two to five moles of hydrogen were usually absorbed before all of the original material was in solution and the products consisted of a mixture of sodium carbonate soluble compounds from which the halogen-free benzyl-benzoic acids were isolated in several experiments in yields varying from a trace to 57% of the calculated amount.

The phthalides from opianic acid with *p*-bromo-*o*-cresol, *p*-bromo-*m*-cresol (condensation *ortho* to the methyl group) and *o*-bromophenol, and from *o*-phthalaldehydic acid with *p*-bromo-anisole, were reduced in this manner and the pure, halogen-free benzyl-benzoic acids isolated. The phthalides from opianic acid with *p*-bromo-*m*-cresol (condensation *para* to the methyl group) and *p*-bromophenol were reduced but only gums isolated. Undoubtedly hydrogenation of the aromatic nuclei also took place to a certain extent in most of the reduction experiments.

Experimental

General Method of Preparation of Phthalides.—The phthalides were prepared by mixing equimolar proportions of opianic acid (or *o*-phthalaldehydic acid) and phenol or phenol ether with sulfuric acid in the proper strength (as given in the table), in the

proportion of 50 cc. of sulfuric acid to 0.1 mole of the phthalaldehydic acid. The sulfuric acid was previously cooled in an ice-salt bath to 0° to prevent the reaction from overheating. External cooling was applied if the temperature of the reaction rose above 25–30°, as a higher temperature led to the deepening of the color of the reaction product and to the formation of a certain amount of by-product.

The reactions were probably complete within an hour but were allowed to stand at room temperature overnight. Ice and water were then added to the reaction mixtures, causing the products to separate either as solids or as gums, as, for example, when phenol, anisole, *m*-cresol or *o*-cresol were used. The crude material was then washed with water.

In the condensation of opianic acid with phenol, anisole, *o*-cresol or *m*-cresol, the opianic acid is added in small portions to a mechanically stirred mixture of the phenol or phenol derivative and the condensing acid. This procedure reduces to a minimum the amount of the by-product formed from two molecules of opianic acid and one of phenol or phenol ether. Because of the slight solubility in the condensing acid this order of mixing is particularly desirable in the case of phenol ethers, so that an excess of opianic acid will never be present to make possible the formation of more by-product.

The phthalides from *p*-bromophenol, *p*-bromo-*o*-cresol, *p*-bromo-*m*-cresol, *o*-bromophenol, *p*-bromo-anisole, *o*-bromo-anisole, *o*-bromo-*o*-cresol, *p*-bromo-*m*-cresol methyl ether with opianic acid and from phenol, anisole and *p*-bromo-anisole with *o*-phthalaldehydic acid were very conveniently prepared by adding the condensing acid to an intimate mixture of the phthalaldehydic acid and phenol, or phenol ether, since the formation of by-products was ordinarily not observed if molecular proportions were used. The reaction mixtures often solidified to a hard cake, which prevented mechanical stirring and made it desirable to use as a reaction vessel an evaporating dish and as a stirrer, a pestle. The reaction products were poured into ice and water and then thoroughly washed.

The very small amounts of by-products formed in the phenol and *m*-cresol condensations were eliminated by four or five crystallizations of the crude product from acetic acid. In the anisole and *o*-cresol condensations, the separation of the by-product was more difficult. The by-products are only slightly soluble in hot alcohol, so that the gummy condensation mixtures were dissolved in this solvent. The solid by-product generally separated directly, particularly if the hot solution was allowed to cool in the presence of seed. Even by this procedure it was impossible to obtain a pure *o*-cresol condensation product, due, probably, to the retention of small amounts of by-product.

The crude reaction products are usually very soluble in most organic solvents, whereas after they are once obtained crystalline they are much less soluble. Crystallization of material from solutions of the crude products was almost invariably slow.

Wherever difficulty was encountered in isolation of the pure products, the details for the procedure used are given below. In the table is a list of the most convenient proportions of solvent for crystallization of relatively pure product, and the recovery is almost always 80–90%. The yields referred to in the tables are also of crystalline material, and this is important because practically quantitative yields of crude product are always obtained. The melting points in all cases are corrected.

5,6-Dimethoxy-2-(2-hydroxyphenyl) Phthalide. II.—The reaction product from 21 g. of opianic acid and 9.8 g. of phenol was thoroughly washed and the gum dried. It was dissolved in 125 cc. of hot glacial acetic acid in the presence of a little Norit and then filtered. Upon standing, crystals were slowly deposited, and crystallization was complete in the course of a day or two. The presence of seed assures a more rapid initial crystallization, but for completion essentially the same time is required as mentioned above. In this way 8.2 g. (29%) of crystalline material was obtained. Another small deposit may be obtained from the filtrate but beyond this, evaporation or cooling yields

no more crystals. The compound is purified from acetic acid (1 g. in 6 cc.) and forms triangular plates; m. p., 177-178°.

TABLE I
PETHALIDES (ALL WHITE)

Name	M. p., °C.	Cond. acid, %	Yield, %	Solvent and proportion	Cryst. form
5,6-Dimethoxy-2-() Phthalide					
1. (2-hydroxyphenyl)	177-8	73	30	Acetic acid (1:6)	Triangular plates
2. (4-methoxyphenyl)	93-5	73	13	<i>n</i> -Butyl ether	Plates
3. (2-methoxyphenyl)	103-4	By methylation	30	Pet. ether and abs. alc.	Prisms
4. (4-hydroxy-3-bromophenyl)	207-8	85	85	Acetic acid (1:14) Alcohol (1:35)	{ Plates (clusters)
5. (2-methoxy-5-bromophenyl)	157-8	85	40	Alcohol (1:40)	Plates
6. (4-methoxy-3-bromophenyl)	136.5-7 ^a	85	97	Alcohol (1:30)	4-Sided plates
7. (4-hydroxy-3-methylphenyl)	185-6	73	42	Alcohol (1:13) Acetic acid (1:9)	{ Plates
8. (3-methyl-4-hydroxy-5-bromophenyl)	163-4 ^b	85	71	Alcohol (1:11)	Thin plates
9. (2-methoxy-4-methyl-5-bromophenyl)	140-0.5	85	83	Alcohol (1:40)	Stout needles
10. (4-hydroxy-2-methylphenyl)	191 5-2.5	73	14	Acetic acid (28%) in toluene (1:25)	Thin plates
11. 2-(4-hydroxyphenyl) Phthalide	155-6	73	79	Acetic acid (28%) in toluene (1:18) Toluene (1:22)	Needles
12. 2-(4-methoxyphenyl) Phthalide	117.5-8.5	73	37	Propyl alc. and water (1:15)	Rectangular plates
13. 2-(2-methoxy-5-bromophenyl) Phthalide	137.5-8.5	85	50	Alcohol (1:28)	Needles

ANALYSES

Formula	Calcd.		Found	
	C	H	C	H
1. C ₁₆ H ₁₄ O ₃	67.11	4.93	66.70	5.01
2. C ₁₇ H ₁₆ O ₃	67.97	5.37	67.61	5.40
3. C ₁₇ H ₁₆ O ₃	67.97	5.37	67.52	5.35
4. C ₁₈ H ₁₈ O ₃ Br	52.60	3.59	52.45	3.62
5. C ₁₇ H ₁₆ O ₃ Br	Br—21.09%		Br—20.92%	
6. C ₁₇ H ₁₆ O ₃ Br	53.82	3.99	53.92	4.22
7. Previously prepared by Jacobson with Adams ^c				
8. C ₁₇ H ₁₆ O ₃ Br	53.82	3.99	53.79	4.10
9. C ₁₈ H ₁₇ O ₃ Br	54.96	4.36	55.07	4.75
10. C ₁₇ H ₁₆ O ₃	67.97	5.37	68.23	5.51
11. C ₁₆ H ₁₄ O ₃	74.81	4.46	74.16	4.64
12. C ₁₈ H ₁₈ O ₃	74.97	5.04	74.67	5.05
13. C ₁₈ H ₁₈ O ₃ Br	56.43	3.48	56.79	3.53

^a Resolidifies and melts at 141°.

^b Resolidifies and melts at 178-9°.

^c Ref. 1 f.

5,6-Dimethoxy-2-(2-methoxyphenyl) Phthalide. XIX.—A solution of 2.5 g. of 5,6-dimethoxy-2-(2-hydroxyphenyl) phthalide in 4 cc. of 10% sodium hydroxide solution was diluted with 25 cc. of water and shaken with 2 cc. of dimethyl sulfate. The

solution was filtered, acidified and the resulting gum dried and washed. Crystallization from dilute alcohol gave 0.75 g. of solid material. This was crystallized by dissolving in a hot mixture of 10 per cent. absolute alcohol in petroleum ether (70–80°). As the solution cooled, a gum separated which was made just to redissolve by addition of a sufficient amount of absolute alcohol. The resulting solution was allowed to stand for two days and large crystals slowly formed. These were filtered and washed with 10% absolute alcohol in petroleum ether. They melted at 102–103°.

A mixture of this substance with 5,6-dimethoxy-2-(4-methoxyphenyl) phthalide, prepared by the condensation of anisole and opianic acid, showed a melting point of 60–70°, thus indicating that they were not identical.

Bromination in glacial acetic acid gave 5,6-dimethoxy-2-(2-methoxy-5-bromophenyl) phthalide, identical with the compound described later that was produced by condensing opianic acid with *p*-bromo-anisole.

5,6-Dimethoxy-2-(4-methoxyphenyl) Phthalide. XX.—The gummy reaction product from 0.05 mole of opianic acid and anisole was dissolved in about 50 cc. of hot alcohol and cooled. Practically all of the by-product present separated and was filtered. The filtrate was evaporated, and the resulting gum washed with 5% sodium carbonate solution, and then treated with a small amount of ether. In this way 2 g. (13%) of a fairly pure product crystallized. The only procedure found for purification was to dissolve in hot petroleum ether (90–110°), and to allow this solution to cool very slowly in the presence of a seed. A crystalline deposit which formed in the course of a day or longer was filtered and recrystallized from *n*-butyl ether, thus giving microscopic crystals melting at 93–95°.

5,6-Dimethoxy-2-(2-hydroxy-5-bromophenyl) Phthalide. III.—A well-stirred solution of 2.77 g. of 5,6-dimethoxy-2-(2-hydroxyphenyl) phthalide in 50 cc. of glacial acetic acid was treated with 2.5 cc. of a molar solution of bromine in acetic acid. Evaporation of the solution gave a quantitative yield of a monobromo derivative which was identical with the material obtained by condensation of opianic acid with *p*-bromophenol.¹⁴

5,6-Dimethoxy-2-(4-hydroxy-3-bromophenyl) Phthalide. VI.—The gummy reaction mixture from 10.5 g. of opianic acid and 4.7 g. of phenol was, without purification, dissolved in chloroform and the solution dried. The cooled solution was then mechanically stirred and 60 cc. of a solution of bromine in chloroform was slowly added. Evaporation of the solvent gave a product which was purified by two crystallizations from alcohol followed by four crystallizations from glacial acetic acid. It was then pure, and melted at 207–208°; it proved to be identical with the compound formed by condensation of opianic acid and *o*-bromophenol.

5,6-Dimethoxy-2-(4-methoxy-3-bromophenyl) Phthalide. XXII.—The crude condensation product from 21 g. of opianic acid and 18.7 g. of *o*-bromo-anisole was diluted with 250 cc. of alcohol and cooled without filtering. The resulting crystalline material was filtered and purified by recrystallization from alcohol (1 g. to 30 cc. of alcohol). The product was obtained in practically quantitative yields and melts at 136.5–137°. It resolidified and melted at 141°. If the temperature of the melting-point bath was raised very slowly, crystallization started again before the first melting was complete, so that the compound appeared to soften at 136.5° and to melt at 141°.

Methylation of 5,6-dimethoxy-2-(4-hydroxy-3-bromophenyl) phthalide with dimethyl sulfate and sodium hydroxide gave this same compound and it showed the same phenomenon of melting and resolidification.

***o*-Bromo-*o*-cresol.**—To 108 g. of *o*-cresol, 154 g. (85 cc.) of 95% sulfuric acid was slowly added with cooling. The solution was heated on a steam cone for 8 hours and then poured onto 300 g. of ice in a 2-liter beaker. To the cold reaction solution, 200 g. of powdered barium carbonate was added, in small portions to prevent excessive

foaming. The excess of barium carbonate and the barium sulfate formed were filtered on a large filter and the colored filtrate containing the barium salt of *o*-cresol-*p*-sulfonic acid was brominated. The barium salt of *o*-bromo-*o*-cresol-*p*-sulfonic acid is so insoluble that it separated and formed in such bulk as to prevent thorough agitation. It was found best, therefore, to brominate one-fourth of the filtrate at a time. Such a portion was diluted to 600 cc., treated with Norit, filtered and 12.5 g. of bromine in 15 cc. of acetic acid was slowly added to the well-stirred solution. External cooling was applied to prevent the temperature from rising above 20°. Even in this dilution the copious separation of the product made very efficient stirring necessary and the last half of the bromine had to be added slowly. The precipitate was filtered in some runs when half of the bromine had been added and the bromination was completed in the filtrate. The barium salt which separated was sucked as dry as possible and then triturated with 200 cc. of alcohol for each 0.25 mole portion. The insoluble salt was filtered, washed with two more portions of 50 cc. of alcohol and dried. The acid filtrate from the bromination retained some material because of the solvent action of the hydrobromic acid. This was recovered by adding 50 g. of barium chloride and allowing it to stand for a day. This precipitate was washed with alcohol, dried and added to the main portion. In this way 68.0–72.6 g. (81–87%) of dry barium salt was obtained.

A mixture of 115 g. of the barium salt with a solution of 344 cc. of 95% sulfuric acid in 400 cc. of water was heated to boiling, and live steam passed through. The *o*-bromo-*o*-cresol distilled and was separated from the aqueous solution with carbon tetrachloride. The fraction boiling at 210–220° at 745 mm. and weighing 38 g. (60%) was redistilled under reduced pressure, boiling at 71–73° (7 mm.).

The *o*-bromo-*o*-cresol has previously been prepared by the decarboxylation of 3-methyl-4-hydroxy-5-bromo-benzoic acid.⁴ It is, however, a very unsatisfactory procedure. An attempt was also made to sulfonate *o*-cresol and brominate the diluted acid solution directly. The difficulty in this procedure, however, consisted in the formation of a certain amount of bromine by the oxidation of the hydrobromic acid by the sulfuric acid. The bromine produced then replaced the sulfonic acid group and the resulting product was, for the most part, dibromo-*o*-cresol. By the isolation of the barium salt of the *o*-bromo-*o*-cresol-*p*-sulfonic acid, no such complication was encountered and a good yield of product resulted.

5,6-Dimethoxy-2-(3-methyl-4-hydroxy-5-bromophenyl) Phthalide. IX.—The crude reaction product from 0.05 mole of opianic acid and *o*-bromo-*o*-cresol was washed with water, then with 100 cc. of cold alcohol and filtered. It was crystallized from 125 cc. of alcohol, giving 13.4 g. of crystalline material. A second crystallization from alcohol gave a pure product, melting at 163–164°, which resolidifies and melts again at 178–179°.

Bromination of the phthalide produced by Jacobson and Adams^{1f} from opianic acid and *o*-cresol gives a compound identical with that prepared above.

5,6-Dimethoxy-2-(4-hydroxy-4-methylphenyl) Phthalide.—The crude material from 0.05 mole of opianic acid and *m*-cresol, using 73% sulfuric acid, was dissolved in 50 cc. of glacial acetic acid and allowed to stand for a week. From the viscous solution crystals slowly deposited, which amounted to 2.1 g. when filtered. These were crystallized once from 25 cc. of acetic acid, giving 1 g. of product, and this was further purified by several crystallizations from a constant-boiling mixture of acetic acid and toluene (28% acetic acid). The pure product melts at 191.5–192.5°.

The structure assigned to this compound was merely assumed.

5,6-Dimethoxy-2-(2-methoxy-5-bromophenyl) Phthalide. XXI.—The crude material from 0.05 mole of condensation product of opianic acid and anisole was dissolved in

⁴ Robertson, *J. Chem. Soc.*, 93, 788 (1908).

50 cc. of chloroform and brominated with 45 cc. of a molar solution of bromine in chloroform. The chloroform was evaporated and the gummy reaction product dissolved in 80 cc. of glacial acetic acid. After standing for a day, 3.1 g. (26%) of crystals deposited, which, when purified by recrystallization from acetic acid, melted at 157–158°.

This compound was identical with that obtained by the bromination of 5,6-dimethoxy-2-(2-methoxyphenyl) phthalide in glacial acetic acid or by the condensation of opianic acid with *p*-bromo-anisole.

bis-(Dimethoxyphthalidyl) Phenols and Phenol Ethers

It was mentioned that in the preparation of phthalides from phenol, anisole, *o*-cresol and *m*-cresol, by-products were obtained in small amounts. These by-products, upon further study, proved to be *bis*-phthalidyl derivatives, and could be made practically the main product of reaction in many cases by modification of the amounts of reacting compound and of the conditions. In particular, the concentration of sulfuric acid for condensing was increased and the proportion of opianic acid to phenol or phenol ethers was doubled.

General Method for Preparation of *bis*-Phthalidyl Compounds.—To a mixture of 0.1 mole of opianic acid in 80 cc. of 95% sulfuric acid was added 0.05 mole of phenol or phenol ether, not allowing the temperature to rise above 30°. In the course of three or four hours the reaction mixture was poured into water and the precipitate filtered. The compounds were purified by crystallization from the solvent indicated in the table. The yields ranged from 25–97% and the products were readily purified because of the fact that the mono-phthalidyl compounds were much more soluble in the solvents used.

TABLE II
Bis-PHthalIDYL DERIVATIVES (ALL WHITE)

Name	M. p., °C.	Yield, %	Solvent and proportion in g.: cc. solvent	Crystalline form
4,6- <i>bis</i> (5,6-dimethoxy-phthalidyl)-				
1. phenol	204.5–6	34	Alcohol (1:65)	Thin plates
2. anisole	210–11	46	Alcohol (1:550)	Long needles
3. 2-methylphenol	205–7	50	Acetic acid (1:20)	Thin, rectangular
			Alcohol (1:46)	needles
4. 3-methylphenol	227.5–9.5		Alcohol (1:85)	Needles
5. 2-bromophenol	215–216 ^a	97	Acetic acid (1:65)	Thin, rectangular needles
6. 4,6- <i>bis</i> (4-bromo-5,6-dimethoxyphthalidyl)-2-methylphenol	266–8 dec.	43	Alcohol (1:700)	Bushy clusters

ANALYSES

Formula	Calcd.		Found	
	C	H	C	H
1. C ₂₆ H ₂₂ O ₅	65.25	4.63	65.12	4.74
2. C ₂₇ H ₂₄ O ₅	65.83	4.92	65.63	4.88
Sap. equiv.		246		248
3. C ₂₇ H ₂₄ O ₅	65.83	4.92	65.50	4.90
4. C ₂₇ H ₂₄ O ₅	65.83	4.92	65.70	5.08
5. C ₂₆ H ₂₁ O ₅ Br	56.00	3.80	55.92	3.80
6. C ₂₇ H ₂₃ O ₅ Br ₂	49.85	3.41	50.38	3.67

^a Resolidifies and melts again at about 224°.

2,4-bis-(5,6-dimethoxyphthalidyl) Anisole. XVIII.—A solution of 1.0 g. of 2,4-bis-(5,6-dimethoxyphthalidyl) phenol (XIII) was dissolved in 10% sodium hydroxide solution and shaken and warmed with 1.5 cc. of dimethyl sulfate. The solution remained clear because of the formation of the carboxyl group from the phthalide group by means of the alkali. Upon acidification, a precipitate formed which was filtered and washed with a 5% sodium hydroxide solution. The insoluble material was crystallized from alcohol and melted at 208–210°.

This product proved to be identical with the bis-dimethoxyphthalidyl compound obtained by the condensation of 2 moles of opianic acid and 1 mole of anisole.

2-Bromo-4,6-bis-(5,6-dimethoxyphthalidyl) Phenol. XVII.—A solution of 2.4 g. of 2,4-bis-(5,6-dimethoxyphthalidyl) phenol (XIII) was dissolved in 100 cc. of hot acetic acid, cooled somewhat and treated with 6 cc. of a molar solution of bromine in acetic acid. There thus precipitated 0.92 g. of the monobromo compound, which was purified by two crystallizations from acetic acid.

This substance was identical with that obtained by condensation of 2 moles of opianic acid with 1 mole of *o*-bromophenol.

4,6-bis-(4-bromo-5,6-dimethoxyphthalidyl)-2-methyl Phenol. XVI.—A mixture of 1.38 g. of 4,6-bis-(5,6-dimethoxy phthalidyl)-2-methyl phenol (XVI) in 50 cc. of acetic acid was refluxed for 2 hours with 7 cc. of a molar solution of bromine in acetic acid. On cooling, there deposited from the solution 0.11 g. of product, and from the filtrate, by evaporation and addition of alcohol, 0.26 g. more was obtained. This was diluted with 20 cc. of alcohol and filtered hot, and the insoluble residue crystallized from 250 cc. of alcohol. In this way 0.12 g. of pure material resulted, melting at 266–268°.

Since the *ortho* and *para* positions in the cresol nucleus were filled, it was assumed that this compound had the formula which has been assigned to it. In other words, the bromines in this case have entered the two opianic acid nuclei. In order to prove this point, 2 moles of bromo-opianic acid were condensed with *o*-cresol, by the general procedure mentioned above, and the same compound was obtained.

Benzyl-Benzic Acids

The method for the reduction of the substituted phthalides to the corresponding benzyl-benzoic acids was essentially the same as that used by Jacobson and Adams.^{1d,e,f}

A mixture of the phthalide (0.05 mole) and 10% sodium hydroxide solution (330 cc. of water and 60 cc. of 50% sodium hydroxide solution) was heated to boiling in a flask fitted with a reflux condenser and a mechanical stirrer. If the phthalide contained no phenolic hydroxyl or was insoluble in the sodium hydroxide solution, the mixture was refluxed until hydrolysis of the inner lactone took place and a clear solution resulted. Zinc dust (60–70 g.) was added to the solution in three or four portions at intervals of an hour. The first portions formed hard balls, but later portions formed a fine suspension of zinc, and the refluxing was continued for 10–20 hours. When the reaction was complete, the zinc was filtered off and the clear, colorless solution was slowly acidified with hydrochloric acid with efficient mechanical stirring. If a pure phthalide had been reduced a crystalline material separated, but it was often difficult to seed the crystallization, and even when seeded it frequently crystallized very slowly and a gum resulted. The gums were best separated with chloroform, the solutions dried and evaporated. The benzyl-benzoic acids from opianic acid were crystallized from toluene, while those from phthalaldehydic acid crystallized best from petroleum ether. The yields given in the table represent those of crystalline material.

During a study of the constitution of various phthalides it was hoped

that catalytic reduction could be employed for the replacement of the halogen in the phthalides by hydrogen. This replacement occurred but it was almost impossible to prevent the reduction from going further, with the formation of benzyl-benzoic acids and in some instances partial hydrogenation of the rings. Those reductions from which solid products were isolated are given below.

TABLE III
BENZYL-BENZOIC ACIDS (ALL WHITE)

Name	M. p., °C.	Yield, %	Solvent and proportion	Crystalline form	Source
5,6-Dimethoxy-2-(4-hydroxybenzyl) benzoic acid	173-4	95	Toluene (1:155)	Needles	Alk. and Cat. red.
2-(2-hydroxybenzyl) benzoic acid	138.5-40	78	Toluene (1:25)	Microcrystals	Alk. red.
3-(4-hydroxy-3-methylbenzyl) benzoic acid	140-2	90	Toluene (1:65)	Plates	Alk. red.
4-(2-hydroxy-3-methylbenzyl) benzoic acid	138.5-9.5	57	Toluene (1:25)	Micro-crystals	Cat. red. Alk. red.
5-(4-methoxybenzyl) benzoic acid					
6-(2-methoxy-4-methylbenzyl) benzoic acid	124.5-6.5	85	Toluene (1:10)	Thick, six-sided plates	Alk. red.
7-(2-hydroxy-6-methylbenzyl) benzoic acid	173-5	21	Toluene (1:130)	Plates	Cat. red.
8-2-(2-methoxybenzyl) benzoic acid	115-6	46	Pet. ether 90-110° (1:60)	Thin plates	Cat. red.

ANALYSES

Formula	Calcd.		Found	
	C	H	C	H
1. $C_{16}H_{16}O_5$	66.64	5.60	66.70	5.78
2. $C_{16}H_{16}O_5$	Previously prepared by Jacobson with Adams			
3. $C_{17}H_{18}O_5$	Prepared by Jacobson with Adams—not purified			
	67.52	6.01	67.49	6.12
4. $C_{17}H_{18}O_5$	67.52	6.01	67.60	6.13
5. $C_{17}H_{18}O_5$	67.52	6.01		
6. $C_{18}H_{20}O_5$	68.32	6.38	67.81	6.25
7. $C_{17}H_{18}O_5$	Previously prepared by Jacobson with Adams			
8. $C_{16}H_{16}O_5$	74.35	5.92	74.68	5.87

Catalytic Reduction of 5,6-Dimethoxy-2-(4-hydroxy-3-bromophenyl) Phthalide.

XI.—A suspension of 2.89 g. of the phthalide in 100 cc. of 95% alcohol was reduced, using 0.1 g. of platinum-oxide catalyst³ and hydrogen under pressure. When the suspended phthalide was all in solution (3 hr., 45 min.), 3.6 molecular equivalents of hydrogen had been absorbed. The reduction was stopped, the catalyst filtered off and the alcohol removed by evaporation. Sodium carbonate dissolved nearly all of the gum, but a small amount (0.01 g.) remained insoluble. This melted at 156-180° and probably consisted mainly of 5,6-dimethoxy-2-(4-hydroxyphenyl) phthalide, but the small yield prevented further investigation. From the sodium carbonate-soluble gum, by crystallization from toluene, a small amount of material (less than 0.01 g.) melting at 171-172.5° was obtained, and this proved to be 5,6-dimethoxy-2-(4-hydroxybenzyl) benzoic acid. No other pure products were isolated.

Catalytic Reduction of 5,6-Dimethoxy-2-(2-hydroxy-3-methyl-5-bromophenyl) Phthalide.

XI.—A suspension of 6.8 g. of the phthalide, prepared as described by Jacobson and Adams,^{1d} in 200 cc. of alcohol was reduced catalytically, using 0.1 g. of catalyst. After 2 hours, the phthalide had all gone into solution, and 2.1 molecular

proportions of hydrogen had been absorbed. Evaporation of the solvent left a gum which partially crystallized. Crystallization from 50% acetic acid gave 3.07 g. of 5,6-dimethoxy-2-(2-hydroxy-3-methylbenzyl) benzoic acid (57%), which had previously been obtained by Jacobson and Adams¹⁴ using zinc and 10% sodium hydroxide as a reducing agent.

Catalytic Reduction of 5,6-Dimethoxy-2-(2-hydroxy-5-bromo-6-methylphenyl) Phthalide.—A suspension of 1.0 g. of the phthalide in 100 cc. of alcohol was reduced, using 0.1 g. of catalyst. The phthalide was all in solution at the end of 2 hours and the reduction was stopped. Evaporation of the alcohol and crystallization of the resulting gum from 10 cc. of toluene gave 0.17 g. (21%) of 5,6-dimethoxy-2-(2-hydroxy-6-methylbenzyl) benzoic acid (melting at 169–171°), which had previously been prepared by Jacobson and Adams.¹⁴

Catalytic Reduction of 2-(2-Methoxy-5-bromophenyl) Phthalide. XXIII.—A suspension of 4.0 g. of the pure phthalide in 100 cc. of alcohol was reduced, using 0.1 g. of catalyst. At the end of 1.75 hours, the material had all dissolved and 2.7 molecular proportions of hydrogen had been absorbed. Partial evaporation of the solvent and addition of water gave 1.4 g. (46%) of crystalline material, which was purified by recrystallization from petroleum ether (90–110°) and proved to be 2-(2-methoxybenzyl) benzoic acid. The pure material melted at 117–118° and was quickly soluble in 5% sodium carbonate solution.

Catalytic Reduction of 5,6-Dimethoxy-2-(2-hydroxy-4-methyl-5-bromophenyl) Phthalide and of 5,6-Dimethoxy-2-(2-hydroxyphenyl) Phthalide gave products from which no solid materials were isolated.

Summary

1. Opianic acid and *o*-phthalaldehydic acid condense with phenol and phenol derivatives to form substituted phthalides which may be converted to anthraquinone derivatives by reduction to substituted benzylbenzoic acids, ring closure and oxidation. This is an important method of synthesizing anthraquinone derivatives of definite structure, if the structure of the substituted phthalides is known with certainty. A study has, therefore, been made of the condensation of opianic acid and *o*-phthalaldehydic acid with phenol and phenol derivatives, and the structure of the resulting products has been demonstrated.

2. The condensation of opianic acid with phenol, anisole, *m*-cresol and *o*-cresol gives mixtures of *o*- and *p*-isomers and the isolation of a pure compound is difficult.

3. The use of bromine to block certain positions in the phenol or phenol derivative restricts or prevents the formation of isomers, and the resulting bromophthalides are also easier to crystallize. If a bromine atom was in the position *ortho* to the hydroxyl or methoxyl, the condensation was directed almost entirely to the *para* position in two cases studied (*o*-bromophenol and *o*-bromo-anisole). If a bromine atom was *para* to the hydroxyl or methoxyl, the condensation took place in the *ortho* position.

4. Attempts were made to remove the bromine from bromophthalides by catalytic reduction. The reductions, however, could not be stopped

at this stage, and as a result the corresponding benzyl-benzoic acids were the only compounds isolated and identified.

5. *o*-Phthalaldehydic acid was condensed with phenol, anisole and *p*-bromo-anisole to give the corresponding substituted phthalides.

6. In the condensation of opianic acid with phenol, anisole, *o*-cresol and *m*-cresol, by-products were formed. These were found to be derivatives of *bis*-phthalidyl phenol, formed by the condensation of two molecules of opianic acid with one of the phenol or phenol derivatives. By varying the conditions these could frequently be made the main product of reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

A STUDY OF THE SYSTEM: ACETANILIDE-PROPIONANILIDE

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Incidental to a study of ketenes, Hurd¹ reports that fractional crystallization of mixtures of acetanilide and propionanilide yields a crystalline material melting sharply at 79.0–79.5°, but states that it is not a definite compound. The behavior would seem to indicate either that the material is a compound or a solid solution, and it was thought by the writers that a study of the freezing-point curves of mixtures of the two substances might furnish additional confirmation of his conclusions.

Experimental

Materials.—Propionanilide was prepared by refluxing redistilled aniline with propionic acid (Eastman Kodak Company). It was recrystallized from alcohol and carbon tetrachloride and melted at 105.0° (corr.).

The acetanilide (Merck) was recrystallized from alcohol, acetone and carbon tetrachloride and froze at 113.6° (corr.).

It was found early in the investigation that very small traces of water had a large effect on the freezing point, though not so much on the customary capillary tube melting point, so the materials were preserved at all times in a vacuum desiccator over sulfuric acid.

Manipulation.—Mixtures of approximately 10 g. each were made up by weight in a large stoppered test-tube, fused and then placed in a Dewar flask filled with hot water. A stirrer and an accurately calibrated thermometer were inserted and the temperature noted while the system cooled. The points at which the first solid phase separated out were obtained with ease and accuracy as there was always a small amount of supercooling, with the resultant rise of temperature. Where the per cent. of either component was large, the system was almost solid at the tem-

¹ Hurd, *THIS JOURNAL*, 45, 3095 (1923).

perature at which the second solid phase appeared and it was difficult to obtain equilibrium conditions and also contact of the mixture with the thermometer. Stirring, such as was permitted by the state of the mixture, aided. Without it the lower points of inflection on the curves fell many degrees too low. No difficulty was experienced with the middle range portions. All temperatures were corrected for emergent stem.

Results

The freezing points of various mixtures are given in Table I and the results are plotted graphically in Fig. 1.

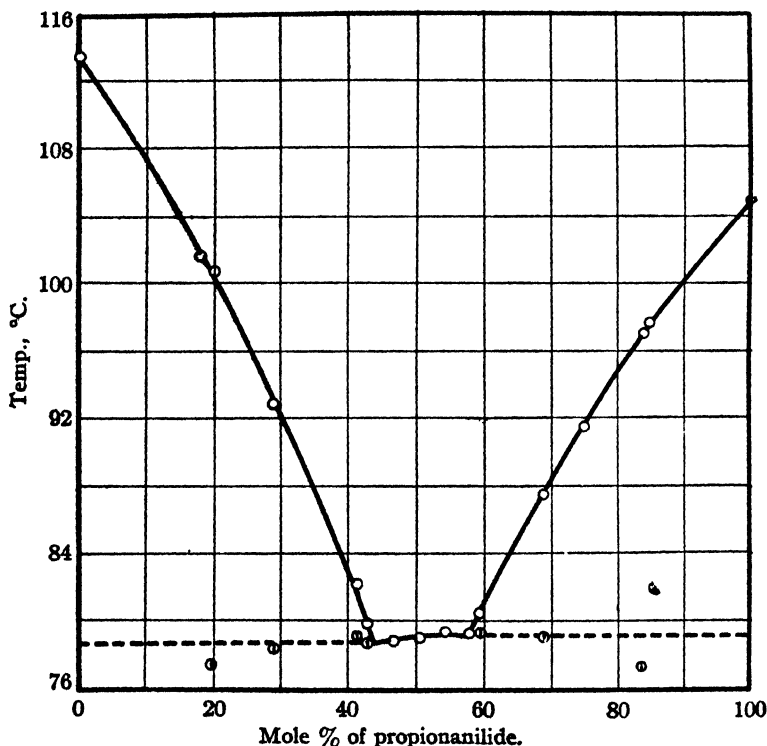


Fig. 1.—Freezing-point composition curves for the system: acetanilide-propionanilide. ○ Freezing points of mixtures. ● Temp. of eutectic halting point.

Discussion

The completed freezing-point-composition curve of the system offers strong evidence of the formation of a compound of the two substances. The central portion is very flat, indicating that the compound is practically completely dissociated in the liquid state. In fact the temperatures along the middle branch of the curve are so close together that the maximum (if any) representing the exact freezing point of the compound cannot

TABLE I
FREEZING POINTS OF MIXTURES OF ACETANILIDE AND PROPIONANILIDE

Mole % of propionanilide	Freezing point, °C.	Temp. of eutectic, °C.
0.0	113.6	..
17.75	101.6	74.2
19.76	100.7	77.5
28.70	92.9	78.4
41.00	82.2	79.2
42.76	79.9	78.8
46.65	78.9	..
50.51	79.1	..
50.93	79.2	..
54.13	79.4	..
48.94	79.1	..
57.85	79.4	..
59.10	80.6	79.4
69.02	88.6	79.2
75.00	91.6	..
83.75	97.1	77.1
84.33	97.7	..
100.00	105.0	..

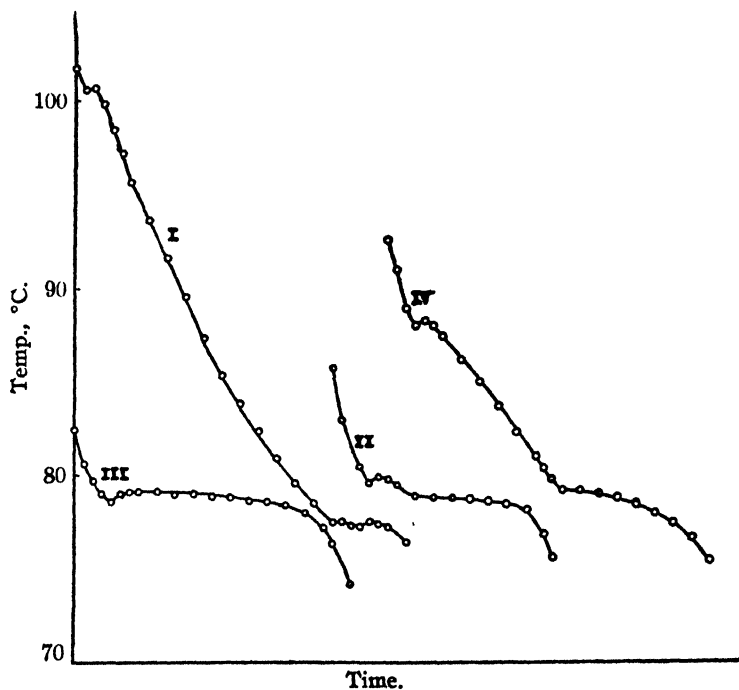


Fig. 2.—Cooling curves. System: acetanilide-propionanilide. Mole % of propionanilide: I, 19.76; II, 42.76; III, 50.51; IV, 69.02. (Curve I made with air cooling.)

be determined accurately. These same temperatures $79.1-79.4^{\circ}$, however, coincide definitely with the melting point reported by Hurd,¹ $79.0-79.5^{\circ}$. From a consideration of the combustion analysis (and other data apparently not included in his article) Hurd concludes that the constant melting substance is a mixture or a solid solution, and the freezing point curve might almost be drawn on that basis, since the central portion is so flat. Consideration of the individual cooling curves (Fig. 2), however, each having two definite breaks, many times with supercooling in each, indicates clearly that in our work we are not dealing with a solid solution but with a compound which forms eutectic mixtures with the pure components. The lower break on each curve occurs within limits of the experimental technique, at the same temperature.

A study of the curves obtained by plotting "eutectic halting time" against composition leads to the conclusion, further, that the system forms no solid solutions, the solid phases consisting of the pure components and the compound.

Summary

1. The freezing-point curves of the system acetanilide-propionanilide have been determined.
2. The presence of a compound, almost completely dissociated in the liquid state, is indicated. The central portion of the curve is so flat that the composition of the compound cannot be determined with certainty.
3. The melting point of the compound is $79.2-79.4^{\circ}$.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

HALOGENATED TERTIARY AMINES

By C. S. MARVEL, W. H. ZARTMAN AND O. D. BLUTHARDT

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A considerable number of halogenated amines are reported in the literature but as a general rule their properties have not been studied in detail. Gabriel¹ has prepared chloro-ethylamine and bromo-ethylamine and has shown that they undergo internal condensations very easily. Knorr² and his students have prepared a few derivatives of the type $XCH_2CH_2NR_2$ and $XCH_2CH_2CH_2NR_2$ and have studied their tendency toward ring formation. The first type forms six-membered piperazine rings and the second type forms eight-membered rings containing two nitrogen atoms. The delta halogenated butylamines have

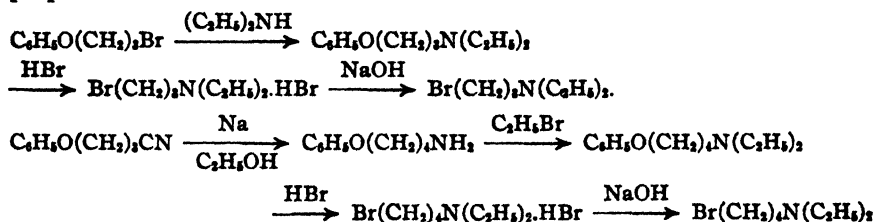
¹ (a) Gabriel, *Ber.*, 21, 567, 574 (1888); (b) 22, 1140 (1889).

² (a) Knorr, *Ber.*, 37, 3511 (1904); (b) Knorr and Roth, *Ber.*, 39, 1424 (1906); (c) Hörlein and Kneisel, *Ber.*, 39, 1429 (1906).

been studied by several investigators³ who have found that they are easily converted to pyrrolidines.

More recently a patent⁴ describing some halogenated propyl- and butyl-diethylamines has appeared. Very little information is given concerning the properties of these compounds. They are said to react as normal alkyl halides in the alkylation of aceto-acetic ester.

From the properties previously recorded for this general class of compounds it was thought that they should be very interesting and useful reagents, if they could be obtained easily. Most of the previous investigators have not given complete directions and yields. Knorr and Roth^{5b} prepared 3-chloropropyl dimethylamine hydrochloride in yields of about 50% by heating 3-phenoxypropyl dimethylamine with concentrated hydrochloric acid in a sealed tube for several hours. We have found that by using hydrobromic acid to open similar ethers, the reactions can be carried out without the use of sealed tubes and yields of 80–88% of the hydrobromides of the bromo-alkylamines can be obtained. In this way 3-bromopropyl diethylamine and 4-bromobutyl diethylamine have been made readily available for use as reagents. The reactions used in the preparation of these two amines are as follows:



All of the reactions proceed smoothly to give good yields except in the case of the isolation of the free amine. There is considerable loss at this stage on account of the rapid formation of quaternary ammonium salt due to internal condensation.

The hydrobromide salts of the halogenated amines are very hygroscopic and very hard to purify. In the open air they take up water so rapidly that it seriously interferes with their purification and analysis. The crude salts can be used in absolute alcohol solution with two moles of sodium malonic ester to give typical malonic ester condensations. These reactions show that these compounds can be used as other alkyl halides in order to introduce the groups $-(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$ and $-(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)_2$.

Experimental Part

3-Phenoxypropyl diethylamine.—To 73 g. of boiling diethylamine in a 500cc. flask fitted with a reflux condenser was added 100 g. of phenoxypropyl bromide over a period

³ (a) Gabriel, *Ber.*, 24, 3232 (1891). (b) Blank, *Ber.*, 25, 3044 (1892). (c) von Braun, *Ber.*, 39, 4121 (1906).

⁴ Eng. pat., 167,781; *Chem. Zentr.* (4), 1921, 1223.

of about thirty minutes. The reaction mixture was heated for about twelve hours when the reaction was complete and the contents of the flask appeared to be almost solid. The reaction mixture was extracted with 200 cc. of ether and the diethylamine hydrobromide was filtered and washed with about 100 cc. of ether. The ether extract and washings were combined and distilled. After the ether was removed, the phenoxypropyldiethylamine was distilled under reduced pressure. The yield was 80–123 g. (84–94% of the theoretical amount); b. p. 147–150° at 20 mm.; d_4^{20} , 0.9425; n_D^{20} , 1.4987. M_p , calcd., 64.39; observed, 64.43.

A small amount of the amine was dissolved in dry ether and converted to the hydrochloride by passing dry hydrogen chloride into the solution. The salt which separated melted at 98–102° with some decomposition.

Anal. (Volhard). Subs., 0.5071 g.: 19.93 cc. of 0.1034 *N* AgNO₃. Calcd. for C₁₁H₂₁ONCl: Cl, 14.56. Found: 14.41.

In a few runs of the amine another substance which was insoluble in ether and only slightly soluble in water was isolated. On recrystallization from hot water this product separated in long, white needles which melted at 77.5–79°. It seemed to be diphenoxypropyldiethylammonium bromide.

Anal. (Volhard). Subs. 0.7000 g.: 16.85 cc. of 0.0981 *N* AgNO₃. Calcd. for C₂₁H₂₅O₂NBr: Br, 18.95. Found: 18.89.

3-Bromopropyldiethylamine Hydrobromide.—A solution of 88 g. of phenoxypropyldiethylamine in 100 cc. of 40% hydrobromic acid was placed in a 500cc. flask, fitted by means of a ground glass connection to a 45cm. fractionating column which in turn was connected with a condenser set for distillation. The flask was placed in an oil-bath heated to 180–210°. Water, hydrobromic acid and phenol distilled from the reaction mixture. More hydrobromic acid was added from time to time until a total of 350–400 cc. was used. It was important to have an excess of hydrobromic acid present at all times as tarry products were formed when the reaction mixture was heated too long without the presence of hydrobromic acid solution. After about twelve to fifteen hours no more phenol came over in the distillate. The residue in the reaction flask was dissolved in about 100 cc. of water and most of the color removed by boiling with decolorizing carbon (Norit). The solution was then evaporated under reduced pressure until all of the water was removed. On standing the residue crystallized slowly. The color varied from gray to brown with different runs. The yield of crude product was about 88 g. (80% of the theoretical amount).

This product was very hygroscopic and attempts to recrystallize the material from solvents were not particularly successful on this account. It was found that dissolving the crude product in absolute butyl alcohol and precipitating with anhydrous ether gave colorless crystals. They were filtered out of contact with air and dried in a desiccator over phosphorus pentoxide and sulfuric acid. There was considerable loss in purification. This product melted at 91–94°.

Anal. (Parr bomb). Subs. 0.3155 g.: 22.88 cc. of 0.1010 *N* AgNO₃. Calcd. for C₇H₁₇NBr₂: Br, 58.18. Found: 57.29.

The low result for bromine was undoubtedly due to the presence of moisture. The range over which the product melted was also probably due to moisture taken up during handling of the product.

3-Bromopropyldiethylamine.—The crude hydrobromide was suspended in ether and this suspension was treated with a large excess of cold, concentrated sodium hydroxide solution. The ether solution was separated, dried over solid sodium hydroxide and the ether distilled under reduced pressure. The residue was distilled at 7 mm. and the fraction boiling at 60–64° was collected. The product came over clear but soon

became cloudy, due to formation of some of the quaternary ammonium compound produced by the reaction of one molecule of the bromo-amine with another. The physical properties and analysis were taken on samples freshly prepared and distilled; d_4^{25} , 1.1524; n_D^{25} , 1.4580. M_D , calcd., 46.40; observed, 45.81.

Anal. (Parr bomb). Subs. 0.8068 g.: 40.43 cc. of 0.1010 *N* AgNO₃. Calcd. for C₇H₁₈NBr: Br, 41.23. Found: 40.19.

On standing overnight the liquid amine changed to a solid quaternary ammonium salt, presumably the eight-membered ring analogous to that which Knorr and Roth^{5b} found to be formed from 3-chloropropyldimethylamine. The salt melted at 180–185° and the bromine could be titrated directly.

Anal. (Volhard). Subs. 0.4002 g.: 20.37 cc. of 0.1010 *N* AgNO₃. Calcd. for (C₇H₁₈NBr): Br, 41.23. Found: 41.12.

Diethyl 3-Diethylaminopropyl Malonate.—In a 1-liter round-bottomed flask connected to a good reflux condenser was placed 500 cc. of absolute ethyl alcohol which had been dried by refluxing with magnesium methyrate and distilling. Through the condenser 15 g. of sodium was added in small pieces as rapidly as possible. When the sodium had reacted, 120 g. of diethyl malonate was added and then a solution of 88 g. of crude bromopropyldiethylamine hydrobromide in 100 cc. of absolute alcohol. The mixture was refluxed for six to eight hours. Sodium bromide separated during this time. Most of the alcohol was distilled and the sodium bromide was dissolved in water. The ester layer was collected in ether and separated from the water layer. The amino ester was extracted from the ether with dilute hydrochloric acid solution, separated from the ether layer and then liberated with alkali. The amino ester was extracted with ether, the ether was distilled and then the residue was distilled under reduced pressure. The product boiled at 163–170° at 23 mm. The yield was 52 g. (62% of the theoretical amount); d_4^{25} , 0.9686; n_D^{25} , 1.4380. M_D , calcd., 74.28; observed, 73.98.

Anal. (Kjeldahl). Subs. 0.4212 g.: 18.08 cc. of 0.1745 *N* HCl. Calcd. for C₁₄H₂₇O₄N: N, 5.12. Found: 5.18.

4-Phenoxybutyldiethylamine.—In a 500cc. flask fitted with a reflux condenser was placed 85 g. of phenoxybutylamine and to it was added 56 g. of ethyl bromide and 21 g. of sodium hydroxide dissolved in 50 cc. of water. The reaction mixture was shaken for a short time. Considerable heat developed. The reaction mixture was allowed to stand for a day and then 56 g. of ethyl bromide and a solution of 25 g. of sodium hydroxide were added. The mixture was again allowed to stand for a day and finally refluxed for about a half hour to complete the reaction. Usually three layers appeared at this stage. The amine layer was on top, the aqueous solution was on the bottom and in between was an oily layer which was probably the quaternary ammonium salt. It was not purified. The amine layer was extracted with ether and the ether distilled. The residue was distilled under reduced pressure and the product boiling at 152–158° at 21 mm. was collected. The yield was 83–91 g. (73–80% of the theoretical amount). Occasionally the yields were higher or lower depending on the amount of quaternary ammonium salt formed; d_4^{25} , 0.9424; n_D^{25} , 1.4975. M_D , calcd., 69.01; observed, 68.51.

4-Bromobutyldiethylamine Hydrobromide.—This product was prepared by the same method used for the corresponding propyl compound. From 100 g. of phenoxybutyldiethylamine and 350 cc. of 40% hydrobromic acid, there was obtained 103–115 g. (79–88% of the theoretical amount) of crude bromobutyldiethylamine hydrobromide. This product was also very hygroscopic and consequently very hard to purify. After crystallizing from anhydrous butyl alcohol and anhydrous ether, crystals which melted at 62–68° were obtained. These were dried in a desiccator over phosphorus pentoxide and sulfuric acid.

Anal. (Parr bomb). Subs. 0.5864 g.: 39.74 cc. of 0.1010 *N* AgNO₃. Calcd. for C₆H₁₁NBr: Br, 55.36. Found: 54.75.

4-Bromobutyldiethylamine.—The free bromo-amine was isolated as described for the propyl compound. It boiled at 68–70° at 6 mm.; d_4^{25} , 1.0187; n_D^{25} , 1.4415. *M_D*, calcd., 52.38; observed, 53.92.

Anal. (Parr bomb). Subs. 0.3197: 15.43 cc. of 0.1010 *N* AgNO₃. Calcd. for C₆H₁₃NBr: Br, 38.46. Found: 38.49.

This amine gradually became opaque and after about twelve hours crystals of the quaternary ammonium compound, which was presumably diethyl pyrrolidinium bromide, began to separate. This product melted at 170–175°.

Anal. (Volhard). Subs. 0.2958 g.: 14.07 cc. of 0.1010 *N* AgNO₃. Calcd. for C₆H₁₃NBr: Br, 38.46. Found: 38.43.

Diethyl 4-Diethylaminobutyl Malonate.—This ester was prepared by the same method used for the corresponding propyl derivative. From 16 g. of sodium, 600 cc. of absolute alcohol, 128 g. of diethyl malonate and 100 g. of crude bromobutyldiethylamine hydrobromide, there was obtained 23 g. (23% of the theoretical amount) of the amino malonic ester, which boiled at 170–175° at 24 mm.; d_4^{25} , 0.9621; n_D^{25} , 1.4468. *M_D*, calcd., 78.90; observed, 80.46.

Anal. (Kjeldahl). Subs., 0.4047 g.: 17.93 cc. of 0.1745 *N* HCl. Calcd. for C₁₆H₂₇O₄N: N, 4.88. Found: 4.90.

Summary

3-Bromopropyldiethylamine and 4-bromobutyldiethylamine have been prepared by general reactions and some of their properties and reactions have been studied.

URBANA, ILLINOIS

[CONTRIBUTION NO. 16 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

ALKYL-NITROGUANIDINES

BY TENNEY L. DAVIS AND STEWART B. LUCE

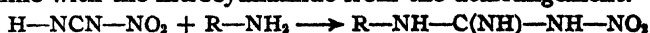
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Nitroguanidine in aqueous solution at 60–70° appears to dearrange in the expected manner¹ to produce, on the one hand, ammonia and nitrocyanamide and, on the other, nitro-amide and cyanamide. If the solution is digested with ammonia, the ammonia inhibits the first of the above-mentioned dearrangements and combines with the cyanamide produced by the second to form guanidine, while the nitro-amide which is liberated at the same time decomposes to produce nitrous oxide, which escapes from the solution. By working with ammonium carbonate, guanidine carbonate is obtained in a yield amounting to 90% of the theoretical, and the by-products are a small amount of melamine from the polymerization of cyanamide, and a smaller amount of urea, from the cyanic acid which results apparently from the loss of nitrous oxide from nitrocyanamide. With aniline a small amount of phenylguanidine is produced, but

¹ Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, 61, 437 (1926).

the principal product is phenylurea. With an aliphatic amine, such as methylamine, a small amount of the alkylguanidine is probably formed, a considerable amount of the alkylurea is produced but the principal product is the alkylnitroguanidine, evidently formed by the combination of the amine with the nitrocyanamide from the rearrangement.



Methyl-, ethyl-, *n*-butyl- and benzylnitroguanidine have been prepared previously and described elsewhere.¹ In the present paper we wish to report a number of other alkylnitroguanidines, and include, for completeness and for comparison, a description of those which have been previously reported. The transformations of these substances are being studied in this Laboratory.

In this work, α -nitroguanidine² was used, for it had been found earlier that both forms of nitroguanidine yield the same methylnitroguanidine. Slightly more than one molecular proportion of nitroguanidine was added to a 10% aqueous solution of the primary amine, and the mixture was heated in the water-bath at 60–70° for 30 or 40 minutes or until almost all of the nitroguanidine had disappeared. Ammonia came off abundantly. The solution was chilled and filtered, and the filtrate was evaporated to dryness in a current of air at laboratory temperature. The combined residues were extracted with dry alcohol at 70° and yielded an insoluble portion which consisted of unchanged nitroguanidine generally associated with considerable amounts of guanidine carbonate, and a solution from which the pure alkylnitroguanidine was obtained by recrystallization, in yields varying from 30 to 50% of the theoretical.

Dimethylamine is the only secondary amine with which we have succeeded in carrying out the reaction. It required more vigorous treatment than the primary amines, a 20% aqueous solution needing about 2 hours' digestion at 70–80° to cause the nitroguanidine to go into solution.

TABLE I
PROPERTIES OF ALKYL-NITROGUANIDINES

Derivative of nitroguanidine	M p, °C.	Crystal habit	Total nitrogen, %		Nitro group nitrogen, %	
			Calcd.	Combustion	Calcd.	Nitrometer
Methyl-	160.5–1.0	Short prisms
Dimethyl-	193.6–4.5	Fine needles	42.42	42.18, 42.40	10.60	10.57, 10.63
Ethyl-	147.0–8.0	Cubes
<i>n</i> -Propyl-	98.0–8.5	Stout needles	38.35	38.45	9.59	9.54
<i>iso</i> Propyl-	154.8–5.6	Cubes	38.35	38.61, 38.45	9.59	9.53
<i>n</i> -Butyl-	84.0–5.0	Stout needles
<i>iso</i> Butyl-	121.0–1.5	Waxy plates	35.00	34.97, 35.16	8.75	8.71, 8.74
<i>n</i> -Amyl-	98.8–9.3	Shiny leaflets	32.18	32.23, 32.22	8.05	8.03, 8.04
<i>iso</i> Amyl-	145.5–6.2	Fine needles	32.18	32.02, 32.17	8.05	8.02, 8.02
<i>tert.</i> -Amyl-	154.8–5.6	Plates	32.18	32.03
Benzyl-	183.5	Needles

¹ Davis, Ashdown and Couch, *THIS JOURNAL*, 47, 1063 (1925).

The alkylnitroguanidines are colorless, crystalline solids, moderately soluble in alcohol, insoluble or slightly soluble in cold water, more soluble in hot, and insoluble or slightly soluble in ether. Benzylnitroguanidine is the least soluble, requiring about 1050 parts of cold water and about 200 parts of boiling water for solution, and is sparingly soluble even in hot alcohol. It chars with concd. sulfuric acid. The others dissolve readily in concd. sulfuric acid, give a blue color with a solution of diphenylamine in that substance, and give up their nitro group nitrogen quantitatively in the nitrometer. They decompose slowly when boiled in aqueous solution.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE CATALYTIC REDUCTION OF *D*-GLUCONIC ACID TO *D*-GLUCOSE

BY J. W. E. GLATTFELD AND EDNA H. SHAVER¹

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The work reported below is an outgrowth of the efforts that are being made in this Laboratory to prepare and study the C₄-saccharinic acids.² This preparation work has now progressed to such an extent that the possibility of extending it to the C₆-saccharinic acids is being considered. This extension would involve as one step the reduction of the C₄-acids to the corresponding aldehydes. The realization of the extension depends, in large measure, on the possibility of discovering a practical procedure for this reduction. Of possible reduction methods the catalytic hydrogenation of the acids in the presence of oxides of platinum seemed to hold promise and the work reported below was done to test it. In order to conserve material, the easily obtained *D*-gluconic acid was used instead of the C₄-saccharinic acids for this preliminary study.

W. E. Cake³ has recently stated that glucose in neutral solution is not reduced by hydrogen in the presence of platinum black. It occurred to us, therefore, that if the reduction of the aldonic acids could be effected by hydrogen in the presence of platinum oxides in neutral or slightly acid solution (that is, with no added acid or very little), the yield of aldoses

¹ The dissertation of which this paper is a condensation was presented by Edna H. Shaver in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in the University of Chicago. Some of the material reported in this paper was presented at the meeting of the Midwest Sections of the American Chemical Society in Chicago, May 27-28, 1927.

² (a) Glattfeld and Miller, *THIS JOURNAL*, 42, 2314 (1920). (b) Glattfeld and Sander, *ibid.*, 43, 2675 (1921). (c) Glattfeld and Sherman, *ibid.*, 47, 1742 (1925). (d) Glattfeld and Woodruff, *ibid.*, 49, 2309 (1927).

³ Cake, *THIS JOURNAL*, 44, 861 (1922).

might be very good because of the fact that the aldoses might not be reduced under these conditions to alcohols.

It was found to be possible to reduce *d*-gluconic acid to *d*-glucose in 14–28% yield (measured as osazone) by this method. A few experiments were tried with mannonic acid and with galactonic acid. With mannonic acid under what seemed to be the same conditions that had proved favorable for the reduction of gluconic acid to glucose, a yield of only 0–2% of mannose (as osazone) was obtained. Galactonic acid in water solution was reduced to dulcitol in 30–45% yield. The conclusion is therefore reached that different aldonic acids require different experimental conditions for successful reduction to the aldoses and, therefore, that the method may prove to be of some value in individual cases with the C₄-saccharinic acids.

Experimental Part

Materials and Apparatus.—The calcium gluconate used as starting material was made by the oxidation of glucose by means of bromine. The purified product showed only a trace of bromide ion, and did not reduce Fehling's solution; analysis for calcium showed it to be practically pure (calcd. for C₁₂H₂₂O₁₄Ca: Ca, 9.31. Found: 9.28, 9.23). The catalyst was prepared by the method of Vorhees and Adams⁴ except that about 0.2 g. of ferrous sulfate per 3 g. of platinum⁵ was added with the sodium nitrate to the chloroplatinic acid solution. The hydrogen used came from a commercial tank of the gas; it was used without purification. The hydrogenating apparatus was that described by Skita⁶ and modified by Vorhees and Adams.⁴

The Procedure.—The sample of calcium gluconate (6.2 g., Col. 2 of table below) was dissolved in about 10 parts of water and such an amount of a sulfuric acid solution (sp. gr. 1.525), (Col. 3) added as to leave the solution finally in the desired condition of acidity with respect to sulfuric acid (Col. 4). The filtrate from the calcium sulfate was concentrated on the water-bath, made up to volume (25 cc.) and the specific rotation determined (Col. 5). The solution was transferred to the reaction bottle, 1 g. of catalyst added and the hydrogenation started. The air was not removed from the reaction bottle before admission of hydrogen.⁷ The bottle was shaken vigorously by a mechanical device for three hours; then another 1g. portion of catalyst was added and the shaking continued for two hours when another 1g. portion of catalyst was introduced and the hydrogenation continued for another two-hour period. The pressure in the reaction bottle slowly dropped during the seven-hour period from 17 pounds to 10. The reaction mixture was then filtered, the volume of the filtrate measured and the specific rotation determined (Col. 6).

Glucosazone.—The reduced reaction solution (from 6.2 g. of calcium gluconate) was made neutral to litmus with sodium hydroxide, and 6 cc. of phenylhydrazine and 4 cc. of glacial acetic acid were added. The customary procedure for osazone formation yielded 4.2 g. of air-dry crystals which were treated with 50 cc. of water. The mixture was heated to boiling and subjected to filtration while hot. The filtrate deposited crystals (Col. 7)

⁴ Vorhees with Adams, *THIS JOURNAL*, **44**, 1402 (1922).

⁵ Carothers and Adams, *ibid.*, **45**, 1071 (1923).

⁶ Skita, *Ber.*, **45**, 3594 (1912).

⁷ Because of the small volume of air in the bottle this seemed a safe procedure in this case; if a large reaction vessel is used the air should be removed before admission of hydrogen because of the possibility of explosion.

which were shown to be the phenylhydrazide of gluconic acid. The material insoluble in the 50 cc. of hot water (Col. 8) was shown to be glucosazone. It was twice recrystallized from 30% alcohol and then melted at 207°, as did also a mixture of this compound with known glucosazone. This fact, together with the analysis of samples (calcd. for $C_{12}H_{22}O_4N_4$: H, 6.19; C, 60.29. Found: 6.19, 6.15, 60.19, 60.23) should be conclusive evidence of the identity of the compound.

This procedure was carried out many times. The table below summarizes the data from six experiments which are fairly representative of the results obtained.

TABLE I
REDUCTION OF *d*-GLUCONIC ACID UNDER 10-17 POUNDS' PRESSURE

Expt. No.	Calcium gluconate, g.	H ₂ SO ₄ , cc. (sp. gr. 1.825)	Theoretical H ₂ SO ₄ if all calcium pptd.	Sp. rot. before reduction	Sp. rot. after reduction	Gluconic phenylhydrazide, g.	Glucosazone, g.	Yield of hydrazide, %	Yield of osazone, %
1	6.2	1.5	0	+12.8	+23.5	2.0	2.1	24.3	20.3
2	6.2	1.5	0	+12.8	+23.5	2.4	2.1	29.1	20.3
3	6.2	1.5	0	+12.8	...	2.5	2.9	30.3	28.1
4	6.2	1.4	Incomplete precipitation	+12.8	+23.8	2.6	2.6	31.5	25.1
5	6.2	1.3	Incomplete precipitation	...	+22.5	2.6	2.6	31.5	25.1
6	6.2	2.0	0.4	3.2	1.5	38.8	14.5

Glucose Oxime.—The gluconic acid obtained from 6.2 g. of calcium gluconate by the addition of the theoretical amount of sulfuric acid was hydrogenated as described above. The filtrate from the catalyst was neutralized with sodium hydroxide and yielded with hydroxylamine 0.15 g. of crystals, m. p. 137°; the melting point of a mixture with known glucose oxime was also 137°.

Isolation and Identification of Glucose

For the isolation of glucose, the filtrate from the catalyst was heated at 100° for half an hour with excess calcium carbonate. The filtrate from the carbonate was concentrated under reduced pressure to a sirup which was repeatedly extracted with boiling absolute alcohol. The alcoholic solution was concentrated under reduced pressure to a sirup, the sirup dissolved in water, the solution again treated with calcium carbonate and the procedure just outlined carried out once more. The alcoholic solution this time was treated with a small amount of ether and allowed to stand for several days with occasional addition of small amounts of ether until such addition caused no further cloudiness. Warty aggregates of crystals appeared on the sides of the test-tubes. The crystals from a large number of such experiments were combined and studied.

Melting Point.—Repeated solution of the crude crystals (m. p. 140°) in absolute alcohol and precipitation with ether yielded crystals which melted at 146°; this melting point could not be raised. A mixture of the purified crystals with anhydrous glucose (m. p. 146°) also melted at 146°.

Rotation.—Four-tenths of a gram of crystals of m. p. 146° in 10 cc. of water solution gave α in a 1-dcm. tube, 20 minutes after solution,

+2.45°; 2 hours after solution, +2.14; 24 hours after solution, +2.08 with no further change in rotation. The corresponding specific rotations are +61.2, +53.5, +52.0. (The equilibrium specific rotation of glucose is +52.6.)

Titration.—Four cc. of the solution used for rotation was made up to 50 cc.; 14.8 cc. of this solution was required for the complete precipitation of the copper in 10 cc. of Fehling's solution of such strength that 10 cc. was equivalent to 0.047 g. of glucose; purity of sample, 99.2%.

Anal. Samples of m. p. 146° were analyzed after repeated purifications by means of solution in absolute alcohol and precipitation with ether. Calcd. for $C_6H_{12}O_6$: H, 6.72; C, 39.97. Found: 6.30, 6.21, 6.18, 6.24, 38.78, 38.87, 38.64, 39.10.

The combustion data were very puzzling in the light of the very good agreement of all other data with those for pure *d*-glucose. The conclusion was finally reached that the impurity present must be an inorganic compound which clung tenaciously to the glucose crystals through all purifications. A sample of 0.4459 g. (m. p. 146°) was ignited, therefore, and found to leave a glassy residue of 0.0100 g. If the impurity were absolutely free from carbon, this small amount of residue might adequately account for the low results of combustion.

Glucosazone from Crystalline Product.—In view of the unsatisfactory combustion results, a characteristic glucose derivative from the crystalline product of the hydrogenation was prepared. From 0.34 g. of crude crystals (m. p. 140°), there was obtained 0.29 g. of crude osazone which, after one recrystallization from 30% alcohol, melted at 207°. This melting point was not lowered by addition of crystals of known glucosazone of m. p. 207°. Furthermore, the analysis of this product gave figures that indicated it to be glucosazone (calcd. for $C_{12}H_{17}O_4N_4$: H, 6.19; C, 60.29. Found: 6.51, 6.34, 60.42, 60.40.).

Summary

The results of a study of the catalytic reduction of *d*-gluconic acid to *d*-glucose in water solution under 10–17 pounds' pressure and in the presence of a platinum oxide catalyst are reported. From the reaction mixture, there was isolated (a) glucosazone in 14–28% yield, (b) glucose oxime and (c) crystalline *d*-glucose.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]
**THE C₄-SACCHARINIC ACIDS. IV. THE PREPARATION OF THE
 TWO *dl*-1,2-DIHYDROXYBUTYRIC ACIDS**

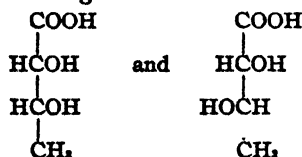
By J. W. E. GLATTFELD AND SYBIL WOODRUFF¹

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As has been stated in previous papers, the preparation of the C₄-saccharinic acids has been undertaken in order to supply data on these acids that may be of value to workers in the sugar field. Our main object, however, has been to supply these data as a preliminary to a study of the mechanism of saccharinic acid formation from the tetroses and other simple sugars, which study it is hoped to make in this Laboratory when the necessary information as to the properties of the theoretically possible products of such action has been obtained.

The work reported in this paper is a continuation of previously reported work. Of the eleven theoretically possible C₄-saccharinic acids (the dihydroxybutyric and -isobutyric acids), the two active 2,3-dihydroxybutyric acids,² the two active 1,3-dihydroxybutyric acids³ and *dl*-1,2-dihydroxyisobutyric acid,⁴ have already been prepared and studied to some extent. This paper reports the preparation of the two *dl*-1,2-dihydroxybutyric acids which have the following formulas:



Discussion of the Literature

None of the work recorded in the literature had as its direct object the study of the acids themselves; their preparation was incidental to other work. Consequently, no thorough comparative study of the acids has been made and the literature leaves the properties and even the separate identities of the two true *dl*-1,2-dihydroxybutyric acids in doubt.

If we pass over the first three papers in the field,⁵ as well as a paper by Faber and Tollens,⁶ we come to two papers by Melikoff⁷ in which reports

¹ The dissertation of which this paper is a condensation was presented by Sybil Woodruff in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the University of Chicago.

² Glattfeld and Miller, *THIS JOURNAL*, **42**, 2314 (1920).

³ Glattfeld and Sander, *ibid.*, **43**, 2675 (1921).

⁴ Glattfeld and Sherman, *ibid.*, **47**, 1742 (1925).

⁵ (a) Melikoff, *Ber.*, **15**, 2586 (1882). (b) Kolbe, *J. prakt. Chem.*, **25**, 369 (1882). (c) Melikoff, *Ber.*, **16**, 1268 (1883).

⁶ Faber and Tollens, *Ber.*, **32**, 2589 (1899).

⁷ (a) Melikoff, *Ann.*, **234**, 197 (1886). (b) Melikoff and Petrenko-Kritschenko, *Ann.*, **266**, 358 (1891).

are made of studies of the chlorohydroxybutyric acids formed by the addition of hypochlorous acid to crotonic and *isocrotonic* acids and of the glycidic (oxygen-ring) and methylglycerinic acids which are derived therefrom. With crotonic acid as starting material, Melikoff isolated crystalline α -chloro- β -hydroxybutyric acid (m. p. 62–63°), crystalline β -methylglycidic acid (m. p. 84°) and crystalline β -methylglycerinic acid (m. p. 80°). *Isocrotonic* acid under similar treatment gave three chlorohydroxybutyric acids of which the one of m. p. 80.5° gave a liquid β -methylisoglycidic acid which, in turn, gave a β -methylisoglycerinic acid of m. p. 45°. Aside from an account of the preparation of the ethyl ester of β -methylglycerinic acid⁸ and an abstract of a paper in the Russian Journal,⁹ no other references could be found to the dihydroxybutyric acids made by the hypochlorous acid method.

One other important method of preparation has been used by two groups of workers. This involves the direct oxidation of salts of the crotonic acids by means of permanganate. Fittig and Kochs¹⁰ obtained by this process an anhydrous dihydroxybutyric acid of m. p. 74–75° and from *isocrotonic* acid a liquid dihydroxybutyric acid. In 1904, Morrell and Hanson¹¹ resolved the β -methylglycerinic acid of Fittig and Kochs, and found the *l*-form to melt at 74–75° and to have a specific rotation in aqueous solution of -13.51° .

It may be said, then, that four presumably different 1,2-dihydroxybutyric acids have been reported in the literature. It is felt that the experimental work reported below definitely establishes the fact that the two *dl*-1,2-dihydroxybutyric acids are those of melting points 81.5 and 74.5°.

Experimental Part

As neither Melikoff nor Kochs records the yields obtained and as Melikoff did not even give quantities of materials used, the details of the published methods had to be worked out and the procedures found by us to give the best results are recorded below. A third method of oxidation—one which yielded the same acid as the permanganate method—was also developed. Finally, a thorough comparative study of the two acids and of some of their derivatives was made in order to establish beyond reasonable doubt the fact that the acids obtained are really different and are the two *dl*-1,2-dihydroxybutyric acids sought.

Preparation of the Acids

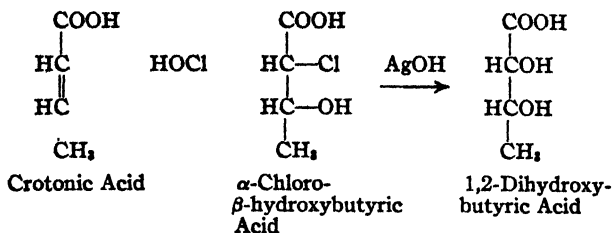
I. The Hypochlorous Acid Method of Preparation.—The essential steps in this method of preparation are indicated below.

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Into a solution of 400 g. of crotonic acid (m. p. 71–72°) in 8 liters of water, mechanically stirred and kept at a temperature of 5–9°, was passed a slow stream of a mixture of chlorine and air (1 to 1) until the reaction mixture no longer decolorized permanganate solution and barely colored a dilute starch-iodide solution (7 to 14 hours; our experiments indicate the longer time is preferable). The solution was concentrated at 25 mm. to 2 liters and divided into 2 equal parts; the history of only one of these is important for this report. This 1 liter of reaction solution was extracted twice with 750 cc. of ether, the ether removed at atmospheric pressure and the residue (368 g. of crude chlorohydroxybutyric acid) in 500 cc. of water treated in the cold with small portions of barium carbonate until effervescence ceased (231 g. of carbonate). The mixture was heated almost to boiling and filtered; the filtrate deposited, in several crops, a total of 375 g. of crude salt (78% of theoretical calculated from crotonic acid). Thirty g. of the barium salt (after one recrystallization) was dissolved in 240 cc. of water and the solution maintained at 70–80° while a water suspension of the silver oxide from 26 g. of silver nitrate was added in very small portions followed by shaking after each addition (two hours for addition). (Great care is necessary during this stage. When most of the silver oxide has been added the silver chloride should be removed, the further addition of oxide made very carefully and the addition stopped when the first appearance of suspended free silver, which gives a pink tinge of translucency to the solution, is noted.) The barium was quantitatively removed from the filtered solution with 8 *N* sulfuric acid and the filtrate from the barium sulfate subjected to distillation to dryness at 25 mm. from a water-bath at 45°. The almost colorless sirup weighed 14.6 g. (84% calcd. from barium salt) and crystallized spontaneously after 24 hours in a desiccator.

The semi-solid mass was transferred to a suction filter and as much liquid as possible removed. A total of 87.0 g. of crude acid thus gave 43.9 g. of fairly dry crystals; m. p., 71–80°. Fourteen g. of these crystals in 5 cc. of water gave, in two crops, 7.3 g. of acid of m. p. 81.5° (the melting point of the acid was very sharp but, because of the very great difficulty in recrystallization, it is possible that the true melting point of the acid may be a little higher). The acid was not hygroscopic, was soluble in alcohol, glacial acetic acid and hot ethyl acetate; insoluble in cold ethyl acetate and ether. The air-dry crystals lost only 0.16% in weight when dried to constant weight over phosphorus pentoxide.

Titration. Subs., 0.2267, 0.4800; 18.94, 39.73 cc. of 0.1 *N* alkali (phenolphthalein). Calcd. for C₄H₅O₄: 18.88, 39.98 cc.

Anal. Subs., 0.1537, 0.1490: H₂O, 0.0918, 0.0898; CO₂, 0.2250, 0.2178. Calcd. for C₄H₅O₄: H, 6.71, C, 39.99. Found: 6.68, 6.74, 39.93, 39.87.

II. The Permanganate Method of Preparation.—To a solution of 20 g. of crotonic acid (m. p. 71–72°) and 22.8 g. of barium carbonate in 200 cc. of water, was added 400 cc. of a saturated solution of barium hydroxide and then 1 liter of water. The milky solution, chilled in ice water, was treated drop by drop with 2 liters of an ice-cold solution of barium permanganate which contained 43.6 g. of the salt; time of addition,

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Preparation of the Acids

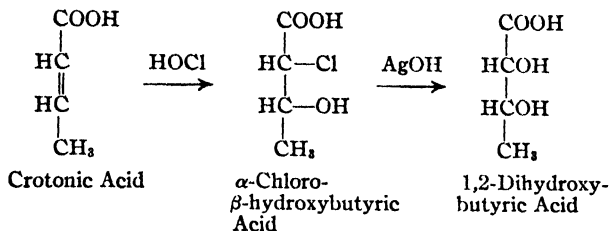
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three hours. The filtered reaction mixture was then concentrated to 800 cc. at reduced pressure from a water-bath at 50–55°, filtered and treated with enough 8 *N* sulfuric acid exactly to precipitate the barium. The filtrate from the barium sulfate was concentrated as above to 200 cc., twice extracted with 150cc. portions of ether, subjected to steam distillation until the distillate became neutral to litmus and subjected to distillation at 15–20 mm. (water-bath at 50–55°) as long as moisture distilled. The sirup thus obtained weighed 7 g. (25% yield) and crystallized within an hour when "seeded" with a crystal of acid made by the osmium tetroxide method (see below).

The 7 g. of acid was recrystallized from 4 cc. of water (solution chilled in ice-salt mixture) and yielded as the first crop 2.3 g. of crystals (m. p., after drying over phosphorus pentoxide, 73.5–74.5°). The air-dry acid was shown to contain 1 molecule of water of crystallization which it lost in a desiccator over phosphorus pentoxide (loss 12.67%). The acid was soluble in alcohol and hot ethyl acetate but insoluble in ether and cold ethyl acetate. The acid, dried over phosphorus pentoxide, was used in the analytical work.

Titration. Subs., 0.2873, 0.3272: 23.92, 27.25 cc. of 0.1 *N* alkali (phenolphthalein). Calcd. for $C_4H_5O_4$: 23.95, 27.27 cc.

Anal. Subs., 0.2901: H_2O , 0.1735; CO_2 , 0.4241. Calcd. for $C_4H_5O_4$: H, 6.71; C, 39.99. Found: 6.65, 39.88.

III. The Osmium Tetroxide Method of Preparation

A solution of 100 g. of crotonic acid (m. p. 71–72°) and 189.2 g. of potassium chlorate in 1500 cc. of water, to which had been added 150 cc. of a water solution of osmium tetroxide which contained about 0.15 g. of the tetroxide, was kept in a water-bath at 50° for eight hours, when a test for completion of reaction was positive. For details of this test, as well as for a complete discussion of this method of oxidation as applied to fumaric and maleic acids, including caution as to the use of osmium tetroxide, the reader is referred to a paper by Milas and Terry.¹² The cooled solution was twice extracted with 500 cc. of benzene in order to remove the catalyst and concentrated at reduced pressure (15–20 mm.) to dryness. The residue was treated with 450 cc. of absolute alcohol, the solution filtered and again concentrated to dryness at reduced pressure. The residue was dissolved in 300 cc. of water and barium carbonate added in slight excess, the mixture heated to boiling, insoluble matter removed and the solution allowed to cool. A total of 156 g. of crude barium salt was thus obtained. Six recrystallizations of this crude salt from water were necessary to remove chloride completely; 76.2 g. of pure salt was obtained which gave, after the removal of barium in the usual way, 24 g. of sirup which crystallized completely when "seeded" (17% yield calcd. from crotonic acid).

The 24 g. of crude crystalline product was recrystallized from 10 cc. of water and yielded 13 g. of acid as a first crop. This acid contained 1 molecule of water of crystallization which it lost to the air in six days (loss 12.82%). The acid, after drying to constant weight in a desiccator over phosphorus pentoxide, melted at 73.5–74.5°. Titration and analysis for carbon and hydrogen gave, in duplicate, results almost identical with those for the acid obtained by the permanganate method.

Derivatives of the Acids

In order to save space the dihydroxybutyric acids prepared by the three different procedures outlined above will be referred to henceforth in this paper as Acid-HOCl, Acid-MnO₄ and Acid-OsO₄, respectively.

¹² Milas and Terry, *This Journal*, **47**, 1412 (1925).

DERIVATIVES OF ACID-HOCl. **Phenylhydrazide**,¹³ C₁₀H₁₄O₃N₂·H₂O.—A mixture of 2 g. of acid (m. p. 81.5°) and 3 g. of phenylhydrazine in 2 cc. of absolute alcohol, warmed for half an hour at 75°, yielded 3.4 g. of crude crystals; twice recrystallized from absolute alcohol these yielded 2 g. of vacuum-dry substance of m. p. 103°. This compound was an ivory-white, granular powder even when it separated slowly from alcohol. Calcd. for C₁₀H₁₄O₃N₂·H₂O: N, 12.28; H, 7.07; C, 52.61. Found: 12.47, 12.25, 7.27, 51.98.

***o*-Tolylhydrazide**, C₁₁H₁₆O₃N₂·H₂O.—This compound was made in the same way as the phenylhydrazide: 2 g. of acid and 3.4 g. of *o*-tolylhydrazine (m. p. 59°) in 4 cc. of absolute alcohol gave 2.9 g. of product; twice recrystallized from 15 cc. of absolute alcohol, this crude product yielded 0.5 g. of substance, m. p. 103°. The compound separated in recrystallizations as a powder. Calcd. for C₁₁H₁₆O₃N₂·H₂O: N, 11.57. Found: 11.52, 11.57.

Barium Salt (C₄H₇O₄)₂Ba.—Three g. of recrystallized acid (m. p. 81.5°) in 7 cc. of water was treated in the cold with 2.4 g. of barium carbonate; the filtered solution was concentrated at reduced pressure to 3 cc. and poured into 25 cc. of absolute alcohol. The precipitated salt was rendered crystalline by trituration in absolute alcohol; 3.5 g. of powdery salt (desiccator-dry) was thus obtained. It could not be recrystallized from water. The salt was dried at 110°. Calcd. for (C₄H₇O₄)₂Ba: Ba, 36.58. Found: 36.16, 36.11.

Silver Salt, C₄H₇O₄Ag.—Three g. of acid (m. p. 81.5°) in 25 cc. of hot water was treated with 3.3 g. of silver carbonate. As the hot filtrate cooled, it deposited 2 g. of white powder. The salt decomposes somewhat if its aqueous solution is heated. Calcd. for C₄H₇O₄Ag: Ag, 47.53. Found: 47.44, 47.42.

DERIVATIVES OF ACID-MnO₄. **Phenylhydrazide**, C₁₀H₁₄O₃N₂·H₂O.—From 2 g. of acid (m. p. 73.4–74.5°) 3.7 g. of white, fluffy, fine needles was obtained; m. p. of purified product, 129.5°. This compound could be recrystallized from 5 parts of absolute alcohol, whereas only 1 part of absolute alcohol could be used with the phenylhydrazide of Acid-HOCl. Calcd. for C₁₀H₁₄O₃N₂·H₂O: N, 12.28; H, 7.07; C, 52.61. Found: 12.31, 12.64; 7.27; 51.53.

***o*-Tolylhydrazide**, C₁₁H₁₆O₃N₂·H₂O.—One and five-tenths g. of acid (m. p. 73.5–74.5°) gave 3.0 g. of product as ivory-white, glistening leaflets. Two recrystallizations from 15 cc. of absolute alcohol gave 1.3 g. of product; m. p., 111.5°. Calcd. for C₁₁H₁₆O₃N₂·H₂O: N, 11.57; H, 7.49; C, 54.52. Found: 11.57, 7.63, 53.69.

DERIVATIVES OF ACID-OSO₄. **Phenylhydrazide**, C₁₀H₁₄O₃N₂·H₂O.—The results of this preparation were identical with those of the preparation of the phenylhydrazide of the Acid-MnO₄ as regards properties of product, behavior and yield. The purified phenylhydrazide melted at 129.5°. Calcd. for C₁₀H₁₄O₃N₂·H₂O: N, 12.28. Found: 12.86, 12.57.

***o*-Tolylhydrazide**, C₁₁H₁₆O₃N₂·H₂O.—This derivative was also similar in method of preparation, yield and properties to that made from the Acid-MnO₄. It melted at 111.5°. Calcd. for C₁₁H₁₆O₃N₂·H₂O: N, 11.57; H, 7.49; C, 54.52. Found: 11.42, 11.39, 7.59, 53.80.

Barium Salt, (C₄H₇O₄)₂Ba.—Five g. of acid (m. p. 74.5°) in 15 cc. of cold water was treated with 4 g. of barium carbonate in portions. The thick paste was heated; the hot filtrate deposited 5 g. of white, needle-like crystals. These were dried at 110°. Calcd. for (C₄H₇O₄)₂Ba: Ba, 36.58. Found: 36.51, 36.62.

¹³ The "phenylhydrazide" obtained here, and likewise from the acids made by the other two procedures, may have been the phenylhydrazine salt of the acid and not the true phenylhydrazide with one molecule of water of crystallization. Because of the stability and general properties of the product, we are inclined to think it was the true phenylhydrazide.

Silver Salt, $C_6H_7O_4Ag$.—A hot solution of 4 g. of acid (m. p. 74.5°) in 50 cc. of water was treated with 4.5 g. of silver carbonate in small portions. The hot filtrate deposited 2 g. of large, glistening, silver-white leaflets. Calcd. for $C_6H_7O_4Ag$: Ag, 47.53. Found: 47.53, 47.64.

Comparison of the Properties of the Acids Made by the Three Different Methods and of their Derivatives

So far as the properties of the Acid- MnO_4 and the Acid- OsO_4 and their derivatives were studied, there is every indication that these acids are identical.

COMPARISON OF MELTING POINTS

Compound	Acid- MnO_4	Acid OsO_4	Mixture of the two
Acid	$73.5-74.5^\circ$	$73.5-74.0^\circ$	$73-74^\circ$
Phenylhydrazide	129.5°	129.5°	129.5°
Tolylhydrazide	111.5°	111.5°	111.0°

The freshly-prepared Acid- MnO_4 lost 12.67% of its weight, the Acid- OsO_4 12.82% as water of crystallization; this corresponds to 1 mole.

In a similar way the Acid- OsO_4 and the Acid-HOCl may be compared and shown to have very different properties.

COMPARISON OF MELTING POINTS

Compound	Acid- OsO_4	Acid-HOCl	Mixture of the two
Acid	$73.5-74.0^\circ$	81.5°	$63-74^\circ$
Phenylhydrazide	129.5°	103.0°	$109-122^\circ$
Tolylhydrazide	111.5°	103.0°	$99-105^\circ$

The Acid-HOCl lost only 0.16% in weight in drying to constant weight and hence contained no water of crystallization. The Acid- OsO_4 was noticeably less soluble in cold water than was the Acid-HOCl. This difference in solubility was sufficiently marked to be of practical importance in the recrystallization of the two acids from water.

The salts of the Acid-HOCl and Acid- OsO_4 exhibited marked differences in behavior. The barium salt of the Acid-HOCl could not be crystallized from water; the barium salt of the Acid- OsO_4 , on the other hand, crystallized from hot water as finely matted, glistening needles. The silver salts of Acid-HOCl and Acid- OsO_4 could both be recrystallized from hot water; the salt of the Acid- OsO_4 consisted of large, glistening, silver-white leaves, however, whereas the salt of Acid-HOCl was obtained as a dull white powder.

The hydrazides (both the phenyl and *o*-tolyl) of the Acid- OsO_4 consisted of definite, large crystals which were sparingly soluble in hot absolute alcohol. The hydrazides of the Acid-HOCl were coarse powders which were markedly more soluble in alcohol than were the hydrazides of the other acid.

Summary

This paper is a report (a) of the repetition, with some modifications, of the preparation of the two *dl*-1,2-dihydroxybutyric acids reported by Melikoff and Fittig and Kochs; (b) of the preparation of one of these acids by a new procedure; (c) of the preparation of two new derivatives (phenylhydrazides and *o*-tolylhydrazides) of each of the two acids; (d) of a careful comparative study of the properties of the acids produced by the three procedures and of a few of their derivatives; and (e) of the con-

clusion that the two theoretically possible *dl*-1,2-dihydroxybutyric acids have melting points of 73.5–74.5 and 81.5°.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF TETRAPHENYL LEAD¹

BY HENRY GILMAN AND JACK ROBINSON

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There are, at present, two general methods for the preparation of tetraphenyl lead. One, by Polis,² is the protracted heating of an ethyl acetate solution of bromobenzene with sodium-lead alloy. The other, by Pfeiffer and Truskier,³ is commonly represented by the following reaction.⁴



The method using the Grignard reagent has been widely employed⁵ because of its greater convenience and better yields. In connection with the application of organolead compounds as antiknock reagents and in the treatment of cancer and some plant diseases, tetraphenyl lead is being used as one of the types for the preparation of variously substituted derivatives. The present study reports the effect of various factors on the yield of tetraphenyl lead as prepared by the Grignard reaction. Using Pfeiffer and Truskier's technique we have not succeeded in equaling their yields. However, the quantity of phenylmagnesium bromide required to give a yield that closely approximates theirs has been significantly decreased below that which they used. Our present maximum yield of about 50% points strongly to a series of reactions more complex than that illustrated in Reaction (1). Experiments have shown that lead chloride cannot be effectively replaced by lead bromide, lead iodide or lead dioxide in this method of preparation. It is possible that better yields may be realized by treating the phenylmagnesium bromide with zinc chloride prior to the addition of lead chloride. Such a method, involving the intermediate formation of organozinc compounds, has been

¹ A preliminary report was read at the meeting of the Iowa Academy of Sciences held at Iowa City on May 6, 1927.

² Polis, *Ber.*, 20, 717 (1887).

³ Pfeiffer and Truskier, *Ber.*, 37, 1125 (1904)

⁴ A recent excellent survey of organolead compounds has been made by Calingaert, *Chem. Reviews*, 2, 43 (1925).

⁵ (a) Hofmann and Wölfl, *Ber.*, 40, 2425 (1907). (b) Möller and Pfeiffer, *Ber.*, 49, 2443 (1916). (c) Jones and Werner, *THIS JOURNAL*, 40, 1257 (1918). (d) Krause and Schmitz, *Ber.*, 52, 2165 (1919). (e) von Hevesy and Zechmeister, *Ber.*, 53, 410 (1920). (f) Richards, King and Hall, *THIS JOURNAL*, 48, 1530 (1926). (g) Ebert, *Ion*, 2, 277 (1910). (h) Staehling, *Compt. rend.*, 157, 1430 (1913). (i) Dillon, Clarke and Hinchy, *Sci. Proc. Roy. Dublin Soc.*, 17, 53 (1922).

used in the preparation of some other organometallic compounds. Probably the optimal conditions described here for the preparation of tetraphenyl lead cannot be used without some variations in the preparation of other tetra-aryl lead compounds, for Krause and Schmitz^{6d} have found that the quantity of "unsaturated" organolead compound increases with more complex radicals like that present in *p*-xylylmagnesium bromide.

Experimental Part

The following directions give the optimum yield, and they incorporate the more desirable features suggested by a limited study of several factors.

Phenylmagnesium bromide is prepared in a three-necked flask from 12.15 g. (0.5 mole) of magnesium, 78.5 g. (0.5 mole) of bromobenzene and 200 cc. of anhydrous ether. When the Grignard reagent has been prepared in the customary manner,⁶ there is added 400 cc. of benzene which has been dried by standing for a few days over sodium. To this solution is added, in one lot, 63 g. (0.23 mole) of finely divided lead chloride,⁷ and the mixture is refluxed, while being continuously stirred, for eight hours.

After a short time (during the first 30 minutes) the characteristic blackish precipitate forms and this increases in quantity over the first four hours. At the end of the eight hour period of refluxing, the mixture is cooled, and then hydrolyzed by pouring into iced hydrochloric acid. The whole mixture is filtered through a Büchner funnel, and then the ether-benzene layer is separated from the dilute hydrochloric acid layer. The cake of tetraphenyl lead, lead, etc., is removed from the funnel (for convenience the filter paper may be removed with the filter cake) and transferred to a beaker or an Erlenmeyer flask. Three hundred cc. of benzene is then added to the cake or paste and heated for a minute or two while the benzene solution is boiling. The hot benzene extract is then separated from the sludge and heavier deposit of lead by filtration and decantation through a Büchner funnel.

The filtrate is cooled with tap water to about 20°, and the crystals of tetraphenyl lead that separate are filtered and set aside as one crop of quite pure tetraphenyl lead, melting at 224–225°. The filtrate, consisting essentially of a saturated solution of tetraphenyl lead in benzene, is then added to the original cake or sludge of tetraphenyl lead and lead already once extracted, and the extraction process repeated by heating at the boiling point of the solvent for a minute or two, and then filtering to get the second crop of tetraphenyl lead. This also is quite pure and melts at about 224°.

This process of extraction is twice repeated (making four extractions in all) in order to remove practically all of the tetraphenyl lead. For most purposes the fourth extraction may be omitted, for on cooling to 20° after the fourth extraction very little tetraphenyl lead separates.

The benzene-extraction mother liquors (now of a volume slightly less than 300 cc.) are combined with the ether-benzene layer that was obtained after the hydrolysis of the reaction mixture. The combined solvents are then concentrated to about 100 cc. and, on cooling these liquors, from 6–10 g. of tetraphenyl lead is obtained melting at 224°.

The total yield of tetraphenyl lead obtained in this way is 29 g. or 50%, based on the lead chloride used. It is pure enough for most purposes. Recrystallization from

⁶ Gilman and McCracken, *THIS JOURNAL*, **45**, 2462 (1923). Using the general procedures described in this reference, one can count safely on a 90% yield of phenylmagnesium bromide.

⁷ The lead chloride used in these studies was taken directly from a stock bottle and was neither pulverized nor dried.

hot benzene gives a product melting at 225°. From 1 to 2 g. of tetraphenyl lead is soluble in 100 g. of benzene at about 20°.

Extraction of the cake or paste may be effected by the use of a Soxhlet apparatus or some modification of it. However, this is not necessary for ordinary purposes. Furthermore, the hot benzene extracts may be filtered conveniently through a Büchner funnel, as stated, without the use of a steam funnel.

Several experiments showed that the yield after refluxing for eight hours is better than that after four, six or twelve hours of refluxing.

The ratio of ether to benzene in the directions given above is about 1 to 2. A lower yield is obtained when two volumes of ether are used to one of benzene.⁸ There is practically no change in yield when benzene is replaced by toluene. When the directions of Pfeiffer and Truskier³ were followed (ether alone as the solvent and an excess of phenylmagnesium bromide) the yield was 43% and not 58.5% as reported by them. This yield of 43% was obtained in one run using the exact amounts of materials recommended by them, as well as in another run twice this size but under the same general conditions.

There is no advantage in using a larger quantity of phenylmagnesium bromide than that stipulated. The directions, therefore, effect a significant saving of RMgX compound.³ With the quantities finally recommended there is still a slight excess of phenylmagnesium bromide, as is shown by the color test of Gilman and Schulze⁹ for RMgX compounds.

It was believed that the yield could be improved by adding the lead chloride in several parts over extended intervals. In this way there was the possibility that the lead chloride would not be so coated with the sludge deposit as to impede reaction with phenylmagnesium bromide. However, there was no improvement in yield when the lead chloride was added in 20 g. portions at either 20 or 30 minute intervals, over that realized when all of the lead chloride was added at one time.

Summary

Improved directions are given for the preparation of tetraphenyl lead from lead chloride and phenylmagnesium bromide.

AMES, IOWA

⁸ Richards, King and Hall (Ref. 5 (f)) found that the substitution of *iso*-amyl ether for ethyl ether was not effective. They also reported that benzene gave more satisfactory yields than ethyl ether.

⁹ Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE REDUCTION OF 2-NITROFLUORENE

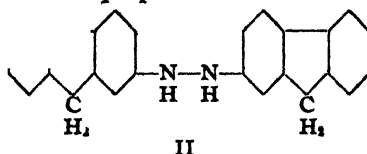
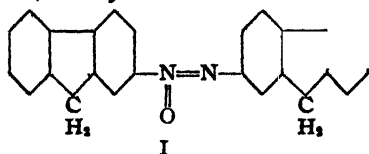
BY F. E. CISLAK, I. M. EASTMAN AND J. K. SENIOR

RECEIVED JUNE 24, 1927

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The reduction of 2-nitrofluorene to 2-aminofluorene has been described by both Strasburger¹ and Diels.² Strasburger carried out the reduction in acid solution by the use of tin and hydrochloric acid; Diels obtained almost quantitative results with zinc and calcium chloride under very nearly neutral conditions. In a recent paper by Korczynski, Karlowska and Kierzek³ appears the statement that 2-nitrofluorene may be easily reduced in alkaline medium to azoxyfluorene (hereafter referred to as 2,2'-azoxybisfluorene), which on account of its great insolubility separates from the solution and thus escapes the further action of the reducing agent. We have been able to find no other reference to this compound in the literature. Since we have prepared it, as well as some of its derivatives, we judge it best to report on the results so far obtained, although the work in this field is not yet complete.

2,2'-Azoxybisfluorene (I) may be prepared by the reduction of 2-nitrofluorene with zinc and calcium chloride. The amount of zinc used, however, is only one-tenth of that used by Diels in his preparation of the amine.



The azoxy compound is a bright orange substance, almost insoluble in alcohol and ether, and only slightly soluble in the higher-boiling organic solvents. It is best recrystallized from boiling xylene in which it is soluble to the extent of about three per cent. When thus treated, it separates in rectangular platelets which melt at 279° (corr.).

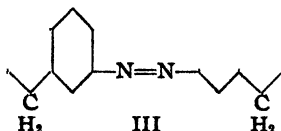
After the empirical formula and molecular weight of the compound had been determined, its structure was demonstrated by reducing it further to 2-aminofluorene. Because of the insoluble nature of the substance, it was necessary to carry out the reduction under special conditions. When the compound was suspended in alcohol, even prolonged treatment with a large excess of zinc and calcium chloride failed to produce more than a slight change. Zinc and acetic acid were also without effect. Success was finally obtained by taking advantage of the solubility of the azoxy compound in phenol. Zinc dust was added to a warm phenol solution of the substance. Then hydrochloric acid was added, and the

¹ Strasburger, *Ber.*, 17, 108 (1884).² Diels, *Ber.*, 34, 1759 (1901).³ Korczynski, Karlowska and Kierzek, *Bull. soc. chim.* (4), 41, 68 (1927).

mixture warmed until all the zinc had dissolved. The deep blue-green color, which appeared as soon as the hydrochloric acid was added to the phenol solution, was bleached during the reduction, and from the reaction mixture 2-aminofluorene was isolated in an amount corresponding to 82% of the azoxy compound used. This result, together with the analysis and molecular weight, is considered to demonstrate the structure of the substance in question.

Attempts were made to oxidize 2,2'-azoxybisfluorene to the corresponding bisfluorenone by treating it with hot chromacetic acid, but even prolonged boiling with this reagent failed to alter the compound—an unusual result in view of the ease with which most fluorene derivatives are converted to fluorenones under these conditions.

During the reduction of 2,2'-azoxybisfluorene to 2-aminofluorene, there was always formed along with the amine a small amount of a white, difficultly soluble substance which, when recrystallized from xylene, formed hexagonal platelets, melting at 257–258° (corr.). By modifying the method of reduction, this compound could be obtained as the principal reaction product. To prepare it, acetic acid instead of hydrochloric acid was used and the reduction was conducted below 45° with as little acid as possible. The compound was at first supposed to be 2,2'-hydrazobisfluorene (II), a supposition with which its analysis and molecular weight agreed; but the behavior of the substance was incompatible with this assumption. In the first place, it obstinately resisted further reduction with zinc and hydrochloric acid even in phenol solution. Under no conditions could it be converted to 2-aminofluorene. Secondly, the compound, when oxidized, yielded only deeply-colored amorphous products. It was impossible to isolate any substance identifiable as 2,2'-azobisfluorene (III) which ought easily to be formed if the compound had the supposed structure.



The most probable alternative hypothesis is that the hydrazo compound really was formed in the course of the reduction, but that, under the influence of the acetic acid, it underwent one of the molecular rearrangements characteristic of compounds of this class. Acetic acid is not a common reagent for producing such rearrangements, but instances of its use for this purpose are known.⁴

Of the five different forms of rearrangement which have been observed⁵

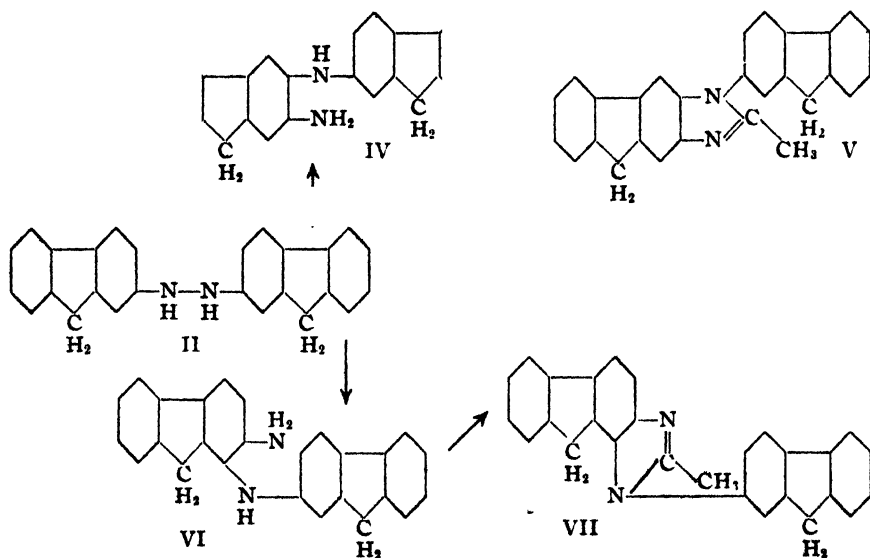
⁴ (a) Meisenheimer, *Ber.*, 36, 4150 (1903). (b) Sachs and Whittaker, *Ber.*, 35, 1433 (1902). (c) Rasso and Rülke, *J. prakt. Chem.* (2) 65, 97 (1902).

⁵ Jacobson, *Ann.*, 428, 81 (1922).

among hydrazo compounds, the benzidine, *p*-semidine, and *o-p*-diphenyloid forms are inapplicable to the present case, because the positions *para* to the hydrazo group are occupied by the bond between the six-membered rings of the fluorene. The remaining two rearrangements (*o-o*-diphenyloid and *o*-semidine) might lead to five different compounds, all isomeric with 2,2'-hydrazobisfluorene.

It was possible to eliminate some of these possibilities by acetylating the compound in question. When treated with acetic anhydride it readily yielded a white derivative which crystallized from xylene in needles melting at 179° (corr.). This compound contained no oxygen and showed by analysis the presence of two more atoms of carbon per molecule than the parent compound. The only simple explanation of these facts is that the acetylated derivative is a C-methyl imidazole. If such is the case, the two nitrogen atoms in the unacetylated compound must occupy two adjacent positions on one phenyl ring, both of them must be amine nitrogens and at least one of them must be primary. Such a configuration is the result of a rearrangement of the *o*-semidine type.

The rearrangement together with the subsequent imidazole formation may be represented by one of the two following schemes.



The two compounds are either 2'-amino-2,3'-difluorylamine (IV) and 3-(2-fluoryl)-2-methyl-2,3-fluorenimidazole (V), respectively, or else they are, respectively, 2-amino-1,2'-difluorylamine (VI) and 1-(2-fluoryl)-2-methyl-2,1-fluorenimidazole (VII). At present, there exist no data which would permit a choice between these two possibilities.

The only property of the unacetylated compound (IV or VI) which is

not in harmony with this interpretation is its weak basic nature. If it does contain a primary amine group it ought to form salts. None such could, however, be obtained in aqueous solution. It is probable that the heavy aryl radicals and extreme insolubility of the substance greatly weaken its basic properties.

Other methods of reducing 2-nitrofluorene were also tried. When boiled in aqueous alcoholic solution with ammonium sulfide, it was not altered. This result is rather curious since the reagent used is very effective in reducing the corresponding 2-nitrofluorenone. When 2-nitrofluorene is treated in methyl alcohol solution with sodium methylate, it yields a brown product which has not yet been fully investigated. It is hoped to identify this substance as well as to find methods of preparing the hydrazo and azo compounds (II and III) which have as yet escaped detection.

Experimental Part

Preparation of 2,2'-Azoxybisfluorene.—2-Nitrofluorene (30 g.) was suspended in one liter of boiling aqueous alcohol (sp. gr. 0.87) to which a solution of 10 g. of calcium chloride in 15 cc. of water had been added. Zinc dust (30 g.) was then added and the mixture refluxed for two hours, cooled and filtered. The cloudy filtrate was then evaporated to small volume and again filtered. The combined precipitates were dried in an oven at 100°. The dried material was treated with about 1500 cc. of boiling xylene, and the hot solution filtered to free it from suspended excess zinc. When the xylene solution was cooled, 2,2-azoxybisfluorene separated in orange-yellow, rectangular plates. The first yield was about 15 g. and an additional 5 g. could be obtained by concentrating the mother liquor. After two recrystallizations from xylene, the substance melted with decomposition at 279° (corr.).

Anal. Calcd. for $C_{26}H_{18}N_2O$: N, 7.49; C, 83.38; H, 4.85. Found: 7.24, 7.45; 83.14, 83.05; 5.10, 5.08.

The molecular weight was determined by the camphor method of Rast.*

Mol. Wt. Calcd. for $C_{26}H_{18}N_2O$: 374. Found: 411, 404, 417.

Reduction of 2,2-Azoxybisfluorene to 2-Aminofluorene.—2,2-Azoxybisfluorene (2 g.) was dissolved in 25 cc. of warm phenol to which zinc dust (5 g.) had been added. Strong hydrochloric acid (20 cc.) was added in small amounts while the mixture was warmed on a hot-plate. By the time the zinc had all dissolved, the deep blue-green color formed when the acid was first added had almost entirely vanished. The entire reaction mixture was poured into water, and sodium hydroxide added in large enough excess to dissolve the zinc hydroxide formed. The insoluble precipitate was removed by filtration and dissolved in alcohol. The filtered solution was poured into excess water and the precipitate removed by filtration. When dried, it weighed 1.65 g., and was identified as 2-aminofluorene. It melted at 124°, and the melting point of a mixture of the compound with 2-aminofluorene (m. p. 129°) was 127°.

The Reduction and Subsequent Ortho-semidine Rearrangement of 2,2-Azoxybisfluorene.—2,2-Azoxybisfluorene (5 g.) was dissolved in 60 cc. of hot phenol. Zinc dust (10 g.) was added and the mixture cooled to 40° while constantly agitated. The azoxy compound separated as a thick paste. Glacial acetic acid (1.75 cc.) was added, a few drops at a time, in the course of about 15 minutes, during which time the mixture

* Rast, *Ber.*, 55, 1051 (1922).

was kept well stirred. The temperature was held below 45°. As the reduction proceeded, the mass became more fluid, and the end of the reaction was marked by the disappearance of the yellow color. The entire reaction mixture was then poured into 1200 cc. of water. The rather oily precipitate became granular when stirred. It was removed by filtration and suspended in 100 cc. of warm alcohol. It was again collected on a filter and then treated with 200 cc. of boiling xylene. The hot xylene solution was filtered to remove excess zinc. When the filtrate was cooled, it deposited a grayish substance, crystallizing in irregular hexagonal scales. This was the substance IV or VI.

As thus prepared the compound contained colored impurities very difficult to remove by recrystallization. It was best purified by dissolving it once more in phenol and treating it with zinc and hydrochloric acid. From the reaction mixture the compound was isolated in the manner already described. After two recrystallizations from xylene, it was obtained in the form of white crystals which, when moist, tended to darken on exposure to the air. The dried compound turned red at 240–245° and melted with decomposition at 257–258° (corr.). The yield was about 50%. The substance is only very slightly soluble in alcohol and ether. It may be recrystallized by adding alcohol to a warm nitrobenzene solution.

Anal. Calcd. for $C_{28}H_{20}N_2$: N, 7.78; C, 86.62; H, 5.60. Found: 7.69, 7.53, 86.85, 86.75, 5.91, 5.84.

The molecular weight was determined by the camphor method.

Mol. Wt. Calcd. for $C_{28}H_{20}N_2$: 360. Found: 312, 330.

Preparation of Compound V or VII.—Compound IV or VI (3 g.) was boiled for two hours with 15 cc. of acetic anhydride. When the cooled reaction mixture was poured into 40 cc. of alcohol, a paste of needle-shaped crystals formed. When dried these melted at 146°. Two recrystallizations from xylene raised the melting point to 179° (corr.), where it remained constant on further recrystallization. The yield was about 65%. The substance is fairly soluble in alcohol, benzene and acetone.

Anal. Calcd. for $C_{28}H_{20}N_2$: N, 7.29; C, 87.45; H, 5.25. Found: 7.26, 7.30, 87.33, 87.83, 5.66.

The molecular weight was determined cryoscopically in benzene.

Mol. Wt. Calcd. for $C_{28}H_{20}N_2$: 364. Found: 437, 438, 438.

Summary

The preparation and properties of 2,2'-azoxybisfluorene are described. This substance may be reduced, but at the same time it undergoes a rearrangement of the *o*-semidine type. The substituted orthodiamine thus formed readily yields an imidazole derivative.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE MECHANISM OF THE REACTION BETWEEN LITHIUM *N*-BUTYL AND VARIOUS ORGANIC HALOGEN COMPOUNDS

BY C. S. MARVEL, F. D. HAGER AND D. D. COFFMAN

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The lithium alkyls are reagents that have not been widely used and many of their reactions have not been thoroughly investigated. It is known that they are spontaneously inflammable in air; that they react with almost any type of organic compound containing oxygen;¹ that they react with water to give the hydrocarbon;² and that they react with quarternary ammonium halides.³ It seemed likely that they might be used to advantage in the synthesis of hydrocarbons by allowing them to react with various halogen derivatives of hydrocarbons. The simple reaction that might be expected would be $RX + LiR' \longrightarrow RR' + LiX$.

In investigating the possibilities of this reaction, lithium *n*-butyl was chosen as a typical lithium alkyl because it is comparatively easy to prepare and is quite soluble in petroleum ether. The lithium *n*-butyl solution was prepared in a large reaction flask, measured, analyzed and then transferred to smaller graduated flasks so that a known amount could be used in each reaction. The halogen compound, usually in solution or suspension in purified petroleum ether, was mixed with the lithium *n*-butyl solution in sealed tubes in such a way that no air was admitted.

The reaction between lithium *n*-butyl and the following halogen compounds was studied: *n*-heptyl bromide, trimethylene bromide, methylene iodide, carbon tetrachloride, β -bromostyrene, tetrachloro-ethylene, *o*-, *m*- and *p*-bromotoluenes, *o*-dichlorobenzene, hexabromobenzene, α -chloropyridine and triphenylchloromethane. With *n*-heptyl bromide, methylene iodide, β -bromostyrene, *p*-bromotoluene and triphenylchloromethane some of the expected hydrocarbon was isolated in each case but the yields varied over a wide range. The other halogen compounds in general gave unexpected compounds or tarry products from which nothing definite could be isolated.

It was noticed in nearly every case that a marked color developed when the lithium *n*-butyl solution and the halogen compound were mixed: This color usually disappeared if the mixture was allowed to stand for several days. The development of color was particularly noticeable when β -bromostyrene was used. When it was first treated with lithium *n*-butyl solution a deep red color appeared. This color changed to a purple and then gradually faded out entirely. When this tube was opened,

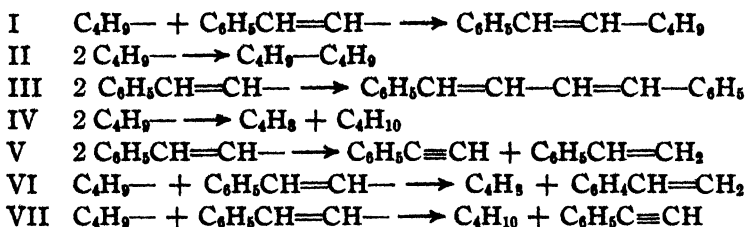
¹ Schlenk and Holtz, *Ber.*, 50, 271 (1917).

² Grosse, *Ber.*, 59, 2653 (1926).

³ Hager with Marvel, *THIS JOURNAL*, 48, 269 (1926).

the products isolated from the reaction were phenyl-1-hexene-1 and *trans-trans*-diphenyl-1,4-butadiene-1,3.

The production of color and the isolation of diphenylbutadiene suggested that probably the reaction between lithium *n*-butyl and β -bromostyrene gave first two free radicals, the *n*-butyl radical and the group $C_6H_5CH=CH-$. These free radicals could then react subsequently in the following manners.




The products isolated indicate that reactions I and III actually had taken place. Probably reaction IV also occurs and the butyl group is lost as gaseous butene-1 and butane. There is no indication that either octane, phenylethylene or phenylacetylene was produced.

If the reaction really proceeds through the formation of free radicals, it would be expected that if lithium *n*-butyl were allowed to react with triphenylchloromethane, the characteristic color of triphenylmethyl would appear. When this reaction was carried out a highly colored solution was obtained. The color deepened on heating the mixture and faded on cooling as it should if hexaphenylethane were produced. When the reaction vessel was opened the color was discharged. The products isolated from the reaction mixture were triphenyl-1,1,1-pentane, triphenylcarbinol and *n*-butyl alcohol. The triphenylcarbinol was a secondary product obtained by the action of sulfuric acid on a mixture of the hydrocarbon and some sulfuric acid soluble product which could not be isolated by crystallization from inert solvents. This substance was presumably triphenylmethylperoxide, the presence of which indicates that a reaction analogous to II above occurred to give hexaphenylethane, which was then oxidized in the air, when the tube was opened, to give the peroxide. The *n*-butyl alcohol must have been formed from a smaller amount of unreacted lithium *n*-butyl by oxidation with air.

The formation of very complex products from compounds containing more than one halogen would be predicted if free radicals are intermediate products in this reaction. Of the polyhalogen compounds studied, only methylene iodide gave enough of the expected hydrocarbon for isolation, and a large high-boiling portion was produced as a side product. *o*-Dichlorobenzene and hexabromobenzene gave very complex insoluble compounds. Trimethylene bromide and carbon tetrachloride gave high-

boiling products from which no definite pure substances could be isolated. Tetrachloro-ethylene was used in only one reaction and when it was mixed with the lithium *n*-butyl solution a very violent explosion occurred.

The only halogen compound used which was not a hydrocarbon derivative was α -chloropyridine. It gave a very tarry product from which nothing definite could be isolated. A free radical of the type  would not be

expected to be very stable.

The products isolated from the reaction of lithium *n*-butyl and *o*-, *m*- and *p*-bromotoluene were the most unexpected. *p*-Bromotoluene and lithium *n*-butyl gave a 76% yield of *p*-*n*-butyltoluene. On the other hand *o*- and *m*-bromotoluenes gave nearly quantitative yields of toluene. In the case of *p*-bromotoluene the reaction is almost entirely of the type illustrated by Equation I. With the *ortho* and *meta* isomers the reaction is almost entirely of the type illustrated by Equation VI. This difference in reaction between *ortho*, *meta* and *para* isomers would not be predicted.

While no butene or butane has been isolated from any of the reaction mixtures, as would be required to establish definitely the exact course of the reaction, there seems to be little doubt that free radicals are first produced when a halogen compound reacts with a lithium alkyl. A very similar mechanism for the Wurtz-Fitting reaction for the synthesis of hydrocarbons has been recently advanced by Bachmann and Clarke.⁴

Experimental Part

Apparatus and General Procedure.—About 1 liter of 1 molar lithium *n*-butyl solution in petroleum ether was prepared and analyzed according to the procedure of Hager and Marvel³ and then transferred from the reservoir C to a series of small reaction flasks as shown in Fig. 1. The reaction flasks were made in two compartments, separated by a glass valve easily broken. In one (D) the lithium *n*-butyl solution was measured. In the other compartment (E) was placed the halogen compound dissolved or suspended in purified petroleum ether. The compartment containing the lithium *n*-butyl solution was sealed off, the glass valve between the two compartments was broken and the two solutions were slowly mixed. In order to avoid accidents the reaction flask was placed behind a heavy glass shield before the valve was broken.

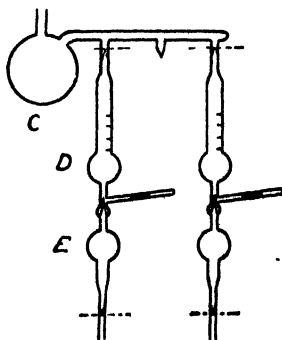


Fig. 1.

⁴ Paper presented before the Organic Section of the American Chemical Society at the meeting in Richmond, April, 1927, *THIS JOURNAL*, 49, 2089 (1927).

The petroleum ether was purified as described in the earlier paper.⁵ The fraction boiling at 35–50° was used. Air was removed from the reaction flasks by displacement with solvent vapors or by evacuating the flask with a mercury vapor pump. All of the liquid halogen compounds were purified by distillation and the material used boiled over only a one-half degree range in most cases. The solid halogen compounds were recrystallized until their melting points were constant.

After the reactions were complete, the reaction flasks were opened and the contents poured into ice water. The aqueous solution was saved and analyzed for halogen and for alkalinity. This gave a rough check on the completeness of the reaction. In nearly every case the reactions ran to completion as far as removal of halogen was concerned. The petroleum ether solutions were carefully distilled and the higher-boiling residues of hydrocarbons were separated as far as possible by distillation or crystallization.

The reaction between lithium *n*-butyl and triphenylchloromethane was carried out in the apparatus shown in Fig. 2. This change in style of apparatus seemed desirable because of the low solubility of the halogen compound in low-boiling petroleum ether. The lithium alkyl solution was placed in one bulb (A) and the dry triphenylchloromethane in the other (B). Some of the petroleum ether was then distilled over into the bulb containing the halogen compound. Some of the triphenylchloromethane dissolved. The apparatus was tilted and this solution was filtered into the lithium *n*-butyl solution. These processes were repeated until all of the triphenylchloromethane was carried into the bulb containing the lithium *n*-butyl.

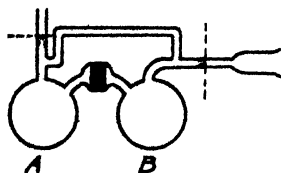


Fig. 2.

Lithium *n*-Butyl and *n*-Heptyl Bromide.—Approximately 0.25 mole of lithium *n*-butyl was mixed with 0.25 mole of *n*-heptyl bromide. After 90 days the tube was opened and the contents poured into ice water. Careful fractionation of the petroleum ether layer resulted in the isolation of 4 g. of nearly pure *n*-undecane. The observed constants were, b. p. 192–197°; d_4^{20} 0.7966, n_D^{22} 1.4220. The constants reported in the literature⁶ are: b. p. 195°; d_4^{20} 0.741; n_D^{20} 1.4184.

Lithium *n*-Butyl and Methylene Iodide.—This reaction was run with 0.50 mole of lithium *n*-butyl and 0.25 mole of methylene iodide. The reaction mixture stood for 23 days before it was opened. About 2 g. of impure *n*-nonane was isolated from a considerable quantity of higher-boiling material which could not be separated into definite fractions. The observed physical constants were: b. p. 147–149°; d_4^{20} 0.7486; n_D^{18} 1.412; whereas those given in the literature⁶ are: b. p. 150.6°; d_4^{20} 0.718; n_D^{20} 1.405.

Lithium *n*-Butyl and β -Bromostyrene.—The reaction was run with 0.25 mole of each reagent. The reaction mixture stood for 38 days before opening. The petroleum ether was distilled under ordinary pressure and then a fraction was removed under

⁵ International Critical Tables, Vol. I. McGraw-Hill Book Co., 1926, page 243.

⁶ Ref. 5, p. 230.

reduced pressure. The residue solidified. The fraction which was distilled under reduced pressure had the following physical constants: b. p. 97–100° at 8 mm.; d_4^{25} 0.9455; n_D^{25} 1.5377; M_p calcd. for phenyl-1-hexene-1, 53.55; found, 52.96.

Anal. (total carbon). Subs. 0.4123: 809.1 cc. CO₂ at 26° and 738.4 mm. Calcd. for C₁₂H₁₄: C, 89.93. Found: 89.65.

The solid residue in the distilling flask was recrystallized from ethyl alcohol and then melted at 145–146°. It added bromine readily to give a product which melted with decomposition at 235–242°. The *trans-trans* isomer of diphenyl-1,4-butadiene-1,3 melts at 147–148° and adds bromine to give a tetrabromo addition product which melts with decomposition at 230°.⁷

Lithium *n*-Butyl and Triphenylchloromethane.—The reaction was run for 9 days using 0.20 mole of triphenylchloromethane and 0.23 mole of lithium *n*-butyl. In working up the product some material crystallized from the petroleum ether. This was separated and found to consist of more than one substance. On treatment with sulfuric acid part of the material went into solution. This was poured into ice water and a solid separated. On recrystallization from alcohol pure triphenylcarbinol melting at 160–161° was obtained. Since the original material would not give triphenylcarbinol on recrystallization alone, this must have been produced from triphenylmethyl peroxide by the action of sulfuric acid.

On distilling the petroleum ether about half a gram of material boiling at 105–116° with the characteristic odor of *n*-butyl alcohol was isolated. Its identification as *n*-butyl alcohol was confirmed by making the 3,5-dinitrobenzoate, which melted at 61°.

The residue after removal of the petroleum ether and *n*-butyl alcohol was distilled under 0.01 mm. pressure and a fraction boiling at 170–180° was isolated. After a few days this fraction solidified and on recrystallization from petroleum ether, acetone or ethyl alcohol gave crystals melting at 153–154°.

Anal. Subs. 0.1642, 0.1680: CO₂, 0.5536, 0.5649; H₂O, 0.1230, 0.1225. Calcd for C₂₂H₂₄: C, 91.94, H, 8.06. Found: C, 92.09, 91.73; H, 8.39, 8.16.

This material is undoubtedly triphenyl-1,1,1-pentane. The total amount isolated was 16 g., or about 26% of the calculated amount.

Lithium *n*-Butyl and α -Chloropyridine.—The quantities used in this experiment were 0.35 mole of lithium *n*-butyl and 0.30 mole of α -chloropyridine. The reaction mixture stood for 7 days. Only tarry, insoluble products could be isolated.

Lithium *n*-Butyl and *o*-Bromotoluene.—A mixture of 0.25 mole of *o*-bromotoluene and 0.27 mole of lithium *n*-butyl was allowed to stand for 4 days. On fractionation of the petroleum ether a 65% yield of toluene boiling at 109–113° was isolated. It was further identified by oxidation to benzoic acid, m. p. 121°, and nitration to 2,4-dinitrotoluene, m. p. 70–71°.

Lithium *n*-Butyl and *m*-Bromotoluene.—A mixture of 0.24 mole of *m*-bromotoluene and 0.25 mole of lithium *n*-butyl was allowed to stand for 4 days. An 87% yield of toluene was isolated.

Lithium *n*-Butyl and *p*-Bromotoluene.—A mixture of 0.25 mole of each reagent was allowed to stand for 30 days. From the petroleum ether was obtained 28 g. (75% of the calculated amount) of *p*-butyltoluene, b. p. 197–200°; n_D^{14} 1.5009; d_4^{14} 0.9452. The constants given in the literature⁸ are: b. p. 198–199°; d_4^{14} 0.8618; n_D^{14} 1.4912. Since the constants did not check as closely as might be desirable, a sample of the hydrocarbon was oxidized to terephthalic acid and this then converted to the dimethyl ester, which melted at 137–138°.

⁷ Rebuffat, *Gazz. chim. Ital.*, 15, 107 (1885); 20, 155 (1890).

⁸ Niemczycki, *Chem. Zentr.*, 71, 468 (1900).

Lithium *n*-Butyl and Polyhalogen Compounds.—When lithium *n*-butyl solutions were allowed to react with trimethylene bromide and carbon tetrachloride, complex liquid hydrocarbon mixtures were obtained. With *o*-dichlorobenzene heavy, tarry products slightly fluorescent in solution were produced. Hexabromobenzene gave a dark insoluble powder. A similar powder was obtained when lithium phenyl was used instead of lithium *n*-butyl. When tetrachloro-ethylene was used a violent explosion occurred.

Summary

1. The reaction between lithium *n*-butyl and various halogen compounds has been studied.
2. In general the simple reaction of replacement of halogen by the *n*-butyl group does not occur.
3. The products which were formed suggest that the first step in the reaction of lithium *n*-butyl and a halogen compound is the formation of free radicals. These then undergo further reactions which differ widely for different groups.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

MAGNESIUM DIETHYL AND ITS REACTION WITH ACETYL CHLORIDE

BY HENRY GILMAN AND F. SCHULZE

RECEIVED JULY 18, 1927

PUBLISHED SEPTEMBER 2, 1927

Introduction

Magnesium diethyl was apparently first prepared by Hallwachs and Schafarik¹ by heating magnesium with ethyl iodide. They described it as a solid, although the reactions of the liquid or oily fraction indicate that some magnesium diethyl was contained in the excess ethyl iodide. Later, Cahours² carried out the preparation from the same materials but he described his product as a liquid. Löhr³ then prepared magnesium diethyl by heating magnesium with ethyl iodide and also by heating magnesium with mercury diethyl. His product was a solid. Fleck⁴ extended Löhr's work on magnesium dialkyls, and, among other reactions, made a careful study of the reaction between magnesium diethyl and acetyl chloride.

We have prepared magnesium diethyl by the preferred method of Löhr³ and Fleck,⁴ namely, by heating magnesium with mercury diethyl

¹ Hallwachs and Schafarik, *Ann.*, 109, 206 (1859).

² Cahours, *Ann.*, 114, 227 (1860).

³ Löhr, *Ann.*, 261, 48 (1891).

⁴ Fleck, *Ann.*, 276, 129 (1893).

in a sealed tube. However, we had no success in a few experiments even when Löhr's directions were carefully followed until a very small amount of mercuric chloride was used as a catalyst.⁵ The magnesium diethyl so obtained was a solid and not a liquid.

Fleck⁴ obtained trimethylcarbinol from the reaction between magnesium *dimethyl* and acetyl chloride. This is exactly as one would expect. However, he got the same carbinol from magnesium *diethyl* and acetyl chloride. This is certainly what one would not expect. Fleck did not expect to get this compound; instead he looked for dimethylethylcarbinol. He was quite aware of the apparently abnormal course of his reaction between magnesium diethyl and acetyl chloride; but there was no doubt in his mind because the product from magnesium diethyl was identical with that from magnesium dimethyl. He repeated the reaction between magnesium diethyl and acetyl chloride several times, and finally "left this quite striking observation unexplained."

In our work with beryllium alkyls, acetyl chloride was used as one of the reagents and it gave the normal or expected products. The same is true with magnesium diethyl, for it has been shown that dimethylethylcarbinol and not trimethylcarbinol is obtained from magnesium diethyl and acetyl chloride.

Experimental Part

It was not found possible to prepare magnesium diethyl by heating magnesium powder with mercury diethyl in an evacuated sealed tube at 130°, even when the heating was continued for 3 days. At a somewhat higher temperature, about 150°, the tube exploded after a short period of heating. However, when fresh mercury diethyl and a small amount of mercuric chloride were heated with magnesium powder at 130° a reaction set in at once. The reaction product was a light gray or brown powder, spontaneously inflammable in the air. On opening the reaction tube there was considerable pressure.

The material was removed from the tubes by dissolving it in 50 cc. of ether. The ether solutions gave a strong positive color test⁶ for reactive organometallic compounds, a test not shown by mercury diethyl. A violent reaction took place when an ether solution of acetyl chloride was added to the magnesium diethyl in ether.⁷ When a negative color test⁶

⁵ The same catalyst has given decidedly successful results in the preparation of organoberyllium compounds. Also, it has been used to bring about reaction between magnesium and some RX compounds that react very slowly with magnesium in ether. Mention of this catalyst, as well as many others, was made in a preliminary paper presented by Gilman, Schulze and Peterson at the Philadelphia, 1926, meeting of the American Chemical Society. The paper has been submitted for publication.

⁶ Gilman and Schulze, *THIS JOURNAL*, 47, 2002 (1925).

⁷ There is no apparent heat of reaction or heat of solution when anhydrous ether is added to magnesium diethyl.

was given (showing that an excess of acetyl chloride was present) the mixture was hydrolyzed by pouring it onto cracked ice containing a small amount of hydrochloric acid. On working up the extract in the customary manner by removing the ether, there remained a liquid with a pronounced camphor-like odor. This distilled between 120 and 125°, with the last portion coming over at about 130°. In order to further characterize this water-insoluble carbinol, it was converted to the corresponding chloride by passing in hydrogen chloride until no more of this gas was absorbed. The methyldiethylchloromethane when distilled in a micro-distillation flask boiled at 115–118°. Its refractive index was 1.4037.

An authentic specimen of methyldiethylcarbinol was prepared from methyl ethyl ketone and ethylmagnesium bromide. It boiled at 120–122°. Treatment with hydrogen chloride gave the methyldiethylchloromethane boiling at 115–118°, and having a refractive index of 1.4034 as determined under the same conditions used for the unknown chloride.

The similarity of the carbinols and the chlorides obtained from them leaves no doubt as to the formation of methyldiethylcarbinol from magnesium diethyl and acetyl chloride.

Summary

Magnesium diethyl prepared by heating magnesium powder with mercury diethyl in the presence of mercuric chloride as a catalyst is a solid and not a liquid. When treated with acetyl chloride it gives methyldiethylcarbinol and not trimethylcarbinol as previously reported.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

A NEW PROCEDURE FOR THE QUANTITATIVE ESTIMATION OF SELENIUM IN ORGANIC COMPOUNDS

BY EDWIN H. SHAW, JR., AND E. EMMET REID

RECEIVED AUGUST 8, 1927

PUBLISHED SEPTEMBER 2, 1927

Introduction

During the recent investigation of some organic selenium compounds the authors¹ felt the need of a simple and direct method of estimating selenium. Most of the methods described in the literature depend on a Carius tube combustion which is slow and tedious. As combustion with sodium peroxide in the Parr bomb has been so successful with sulfur,² and has supplanted the Carius method with halogens,³ it seemed advisable to adapt this method to the determination of selenium. The only novelty is in the use of the fusion method. Two commonly used methods have

¹ Shaw and Reid, *THIS JOURNAL*, **43**, 320 (1923).

² Parr, *ibid.*, **30**, 763 (1906).

³ Lemp and Broderick, *ibid.*, **39**, 2069 (1917).

been employed for the determination of the selenium in the solution of the melt.

Historical

Siemens⁴ determined selenium in ethyl selenomercaptan by passing its vapors over hot copper oxide and noting the change in weight, $\text{CuO} \rightarrow \text{CuSe}$. Michaelis and Röhmer⁵ heat the compound in a bomb tube with fuming nitric acid, reflux the product with excess hydrochloric acid to remove the nitric acid, and precipitate elementary selenium from the resultant solution with sodium sulfite. Bauer⁶ describes a similar process. Lyons and Shinn⁷ modify the elimination of the nitric acid by evaporating the solution to dryness with the addition of silver nitrate or zinc nitrate to prevent loss of selenious acid. The product is dissolved in dilute hydrochloric acid, and either titrated with thiosulfate or precipitated with sodium sulfite. Frerichs⁸ oxidizes in the same way but converts the selenium into silver selenite, and determines silver volumetrically as a measure of the selenium present, while Becker and Meyer⁹ weigh the silver selenite formed. Wrede¹⁰ burns the compound in oxygen in the presence of platinum as a catalyst, and titrates the selenious acid formed with centi-normal sodium hydroxide, sodium acid selenite being neutral to methyl orange.

Results

The procedure which was arrived at after many variations of the conditions, and which gave satisfactory results with all the compounds tried, was as follows. Mix the weighed sample, 0.2 to 0.4 g., with 0.4 g. of cane sugar, 0.2 g. of potassium nitrate and 14 g. of sodium peroxide and spread a thin blanket of sodium peroxide over the charge. The combustion is made in the usual manner. The melt is dissolved in water, boiled to destroy hydrogen peroxide, cooled, acidified with hydrochloric acid, filtered and diluted to 350 cc. The selenium in this solution is in the form of selenic acid, and is not reduced to the free elementary form by passing sulfur dioxide through the solution. From this solution the selenium may be precipitated by two alternative methods.

1. **Precipitation by Sulfur Dioxide.**—The sulfur dioxide precipitation was first described by Rose.¹¹ This method has the advantage of rapid and complete precipitation, and the disadvantage of possible loss of the

⁴ Siemens, *Ann.*, 61, 360 (1874).

⁵ Michaelis and Röhmer, *Ber.*, 30, 2827 (1897).

⁶ Bauer, *Ber.*, 48, 507 (1915).

⁷ Lyons and Shinn, *THIS JOURNAL*, 24, 1087 (1902).

⁸ Frerichs, *Arch. Pharm.*, 240, 656 (1902).

⁹ Becker and Meyer, *Ber.*, 37, 2551 (1904).

¹⁰ Wrede, *Z. physiol. Chem.*, 109, 272 (1920).

¹¹ Rose, *Pogg. Ann.*, 113, 472; *Z. anal. Chem.*, 1, 73 (1862).

volatile selenium monochloride from the hot solution.¹³ This loss can be reduced by shortening the time of heating the selenic acid with excess hydrochloric acid and by using a rapid stream of sulfur dioxide to bring about the reduction. To the 350 cc. of solution obtained above, 200 cc. of concentrated hydrochloric acid is added, and the solution covered with a watch glass and brought to the boiling point. Sulfur dioxide is passed into the hot, but not boiling, solution until the precipitate has entirely coagulated and the supernatant liquid is clear. The watch glass is rinsed into the solution and 200 cc. of water are added to the solution. The precipitated selenium is filtered through a Gooch crucible, the beaker is rinsed with alcohol to remove traces of adhering selenium and the precipitate is washed with alcohol and finally several times with water. The Gooch crucible is dried at 110–120° and weighed.

2. **Precipitation by Potassium Iodide.**—The potassium iodide precipitation has been described by Peirce.¹³ By this method the reduction of selenates is not complete unless all the iodine is boiled out of the solution, and in the presence of excess iodine some of it is strongly adsorbed by the selenium. The continued boiling of the solution to expel the iodine may lead to mechanical loss of selenium. Care to prevent too vigorous boiling will prevent this mechanical loss. To the 350 cc. of solution obtained above, 50 cc. of concentrated hydrochloric acid is added and 3 g. of potassium iodide. Boil the solution gently to remove the iodine, replacing the water lost by evaporation. This boiling out requires about two hours. The selenium is then filtered through a Gooch crucible, the beaker is rinsed with alcohol to remove traces of adhering selenium and the precipitate is washed with alcohol and finally several times with water. The Gooch crucible is dried at 110–120° and weighed.

Experimental

The organic selenium compounds used to demonstrate this analytical method are described in a previous paper by the authors.¹ Another compound was used, *p*-nitrophenylselenocyanate prepared by the method of Bauer.¹⁴ As described by Bauer, the compound is not pure, being colored light brown and melting at 136.7–137.3° (corr.). The product can be purified by dissolving in concentrated nitric acid and precipitating by the addition of water. It crystallizes in thin leaves, has a very slight yellowish color and melts sharply at 139.4° (corr.). An additional recrystallization by dissolving in concentrated nitric acid and adding water did not increase the melting point, the product melting simultaneously with the original material at 139.4° (corr.). Recrystallization from water,

¹³ Lenher and Kao, *THIS JOURNAL*, 47, 2454 (1925).

¹³ Peirce, *Z. anorg. Chem.*, 12, 409 (1896).

¹⁴ Bauer, *Ber.*, 46, 95 (1913).

in which the compound is sparingly soluble, produced no improvement, the product melting at 139.4° (corr.).

Table I gives results obtained in the analysis of ethyl seleninic acid hydronitrate and *p*-nitrophenylselenocyanate by means of the sulfur dioxide precipitation described above.

TABLE I
ANALYSES BY SO_2 PRECIPITATION

Compound	Weight of sample	Selenium, weight			Selenium, per cent.		
		Theory	Found	Error	Theory	Found	Error
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$	0.1917	0.0743	0.0741	-0.0002	38.77	38.65	-0.12
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.1798	.0697	.0695	-.0002	38.77	38.65	-.12
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.2741	.1063	.1063	.0000	38.77	38.77	.00
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.3380	.1310	.1308	-.0002	38.77	38.70	-.07
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.3986	.1545	.1552	+.0007	38.77	38.94	+.17
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.3723	.1443	.1436	-.0007	38.77	38.57	-.20
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.6218	.2411	.2403	-.0008	38.77	38.65	-.12
$\text{C}_2\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.5666	.2197	.2192	-.0005	38.77	38.69	-.08
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{SeCN}$.2153	.0750	.0746	-.0004	34.85	34.65	-.20
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{SeCN}$.2160	.0753	.0752	-.0001	34.85	34.81	-.04

Table II gives results obtained in the analysis of *p*-nitrophenylselenocyanate by the potassium iodide precipitation described above.

TABLE II
ANALYSES OF *p*-NITROPHENYLSELENOCYANATE BY KI PRECIPITATION

Weight of sample	Selenium, weight			Selenium, per cent.		
	Theory	Found	Error	Theory	Found	Error
0.2340	0.0815	0.0817	+0.0002	34.85	34.91	+0.06
.2615	.0911	.0908	- .0003	34.85	34.72	- .13
.2533	.0883	.0877	- .0006	34.85	34.62	- .23
.2077	.0724	.0717	- .0007	34.85	34.52	- .33
.2410	.0840	.0833	- .0007	34.85	34.56	- .29

Table III is a collection of results previously published,¹ included here to show the applicability of the analytical method to an assortment of compounds. These compounds represent all the solid compounds described in the previous paper.

TABLE III
RESULTS PREVIOUSLY PUBLISHED, PRECIPITATION BY SO_2

Compound	Weight of sample	Selenium, weight			Selenium, per cent.		
		Theory	Found	Error	Theory	Found	Error
$\text{C}_6\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$	0.4463	0.1730	0.1721	-0.0009	38.77	38.56	-0.21
$\text{C}_6\text{H}_5\text{SeO}_2\text{H} \cdot \text{HNO}_3$.4886	.1894	.1896	+.0002	38.77	38.80	+.03
$\text{C}_6\text{H}_5\text{SeO}_2\text{H} \cdot \text{HCl}$.4001	.1783	.1778	-.0005	44.56	44.44	-.12
$\text{C}_6\text{H}_5\text{SeO}_2\text{H} \cdot \text{HCl}$.4198	.1871	.1865	-.0006	44.56	44.42	-.14
$\text{C}_6\text{H}_5\text{SeBr}_2$.3805	.0866	.0867	+.0001	22.76	22.79	+.03
$\text{C}_6\text{H}_5\text{SeBr}_2$.4160	.0947	.0945	-.0002	22.76	22.72	-.04
$\text{O}_2\text{S}(\text{C}_6\text{H}_4\text{SeC}_6\text{H}_5)_2$.4376	.2059	.2063	+.0004	47.05	47.14	+.09
	.4601	.2165	.2167	+.0002	47.05	47.10	+.05
$\text{C}_6\text{H}_5\text{Se}-\text{C}_6\text{H}_4\text{O}_2-\text{SO}_2\text{C}_6\text{H}_5$.4125	.0750	.0763	+.0013	18.19	18.49	+.30
	.3847	.0700	.0701	+.0001	18.19	18.22	+.03

Acknowledgment

The authors wish to acknowledge their indebtedness to the late Professor Victor Lenher of the University of Wisconsin and to Dr. S. J. Dickinson of the American Smelting and Refining Company for valuable suggestions as to the precipitation of selenium from selenates by the potassium iodide method.

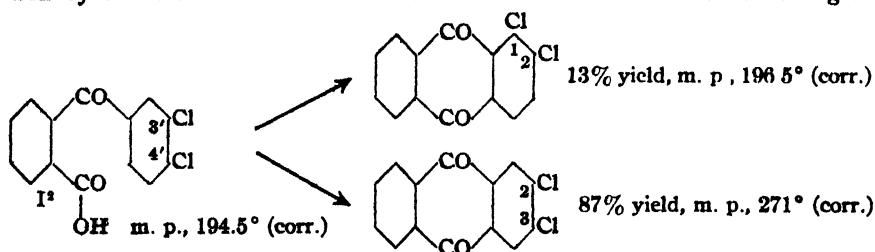
Summary

The Parr bomb fusion method has been adapted to the analysis of organic selenium compounds. The conditions for the precipitation of the selenium from the solution of the melt have been worked out.

BALTIMORE, MARYLAND

NOTES

The Formation of 1,2-Dichloro-anthraquinone and 2,3-Dichloro-anthraquinone from *o*-Dichlorobenzene.—Phillips states¹ that dichlorobenzoylbenzoic acid of the constitution shown in Formula I does not give



any 1,2-dichloro-anthraquinone on condensation with concentrated sulfuric acid. This statement is erroneous as I have shown² that there is always formed about 13% of 1,2-dichloro-anthraquinone, which remains in the sulfuric acid after the condensation and crystallizes on diluting the acid in little leaflets. The substance melts, contrary to the statement of Ullmann,⁴ at 196.5° (corr.), and not at 207°.

I may add that Phillips' observations are, on the other hand, quite in agreement with ours.³ The 1,2-dichlorobenzene was quite pure, being especially made for us by the Aktiengesellschaft für Aniline Fabrikation in Berlin. I have already published this fact on page 488 of my "Künstliche Organische Farbstoffe" (Berlin, 1926). The yield of the 3',4'-dichlorobenzoylbenzoic acid was in our best experiments 35%.⁵

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HANS EDUARD FIERZ-DAVID

RECEIVED JUNE 2, 1927
PUBLISHED SEPTEMBER 2, 1927

¹ Phillips, *THIS JOURNAL*, 49, 473-478 (1927).

² The sodium salt as well as the potassium salt is sparingly soluble.

³ E. Senn, *Dissertation*, Swiss Technical High School, 1923.

⁴ See Ullmann, *Encyklopaedia*.

⁵ Ref. 3, p. 29.

Note.—The work of Emil Senn upon which Professor Fierz-David bases his objection to a statement which occurs in my paper (THIS JOURNAL, 49, 473 (1927)) unfortunately was never published in any chemical journal, nor have I been able to find any reference to it or abstract of it in *Chemical Abstracts*, *Chemisches Zentralblatt* or in the *British Chemical Abstracts*. I learned of this work quite recently and have since carried out the condensation of 3',4'-dichloro-2-benzoylbenzoic acid according to the directions given in Senn's dissertation and succeeded in obtaining 4% of the total yield of 1,2-dichloro-anthraquinone. The inference that one might draw from the statement in my paper that no 1,2-dichloro-anthraquinone is formed in this condensation is therefore incorrect and I wish to correct it accordingly. I may add, finally, that in my experiments the yield of 3',4'-dichloro-2-benzoylbenzoic acid was invariably 70% or better.

M. PHILLIPS

RECEIVED AUGUST 8, 1927
PUBLISHED SEPTEMBER 2, 1927

NEW BOOKS

General Inorganic Chemistry. By M. CANNON SNEED, Professor of Chemistry, University of Minnesota. Ginn and Company, 15 Ashburton Place, Boston, 1926. vi + 674 pp. 132 figs. 21.5 × 14.5 cm. Price, \$3.00.

In this textbook, written for students beginning a college course in chemistry, descriptive and theoretical matter are well balanced, probably more so in the first thirty-one chapters than in the remaining fifteen, which are given over largely to descriptive matter on the metals; but in this latter part we find special coördinating chapters on "Ionic Equilibria," "Colloids," "Chemistry in Living Processes" (written by R. A. Gortner), "Electrochemistry" and "Radioactivity." In arrangement and method of presentation, the author has followed a conservative course. Modern theories and recent industrial applications, however, have not been neglected. The structure of the atom is adequately presented in the splendid chapter on "The Periodic System," and the electron concept as applied to chemical changes is clearly and fully illustrated by well-chosen examples in the chapter on "Oxidation and Reduction."

The style is clear; fundamentals are emphasized by a judicious use of heavy type; misprints and mistakes are very rare; the format is of high standard; most of the diagrams of apparatus show complete set-ups; the illustrations include twelve full-page portraits of noted chemists; the historical matter interspersed adds interest and introduces the human element; nearly every chapter is closed with a limited but well-chosen set of questions and exercises of the type which require careful thought and induce discussion in class conferences; a serious, scientific tone

pervades the book; it deserves rank in the group of up-to-date and scholarly texts for first-year work in general chemistry—new and revised—which have appeared within the past three years.

Other distinctive and valuable features are: A model study outline at the end of Chapter II, "Oxygen and Ozone," helpful both to student and instructor. Much information for reference use is incorporated in the 67 tables, for example, Clarke's full table showing abundance of common elements, p. 17; activity of metals, p. 50; critical temperatures and pressures, p. 107; solubilities of some inorganic substances, p. 197; types of organic compounds, p. 424; composition of alloys (3 tables); silicic acids and their salts, p. 431; constants of metals, pp. 442–443; etc. The chemical equation and heat changes are illustrated in the chapter on "Thermochemistry."

Small volumes are expressed in ml. and not cc. As new terms in elementary texts we note: reactants, dissociants, electrovalence, covalence, monosilane, disilane, electrodialysis, heterocyclic compounds. The millimicron is defined correctly, p. 554, but is designated by the symbol for the micromicron. The use of exact atomic weights is stressed in the chapter on "Calculations" by expressing atomic weights to the third decimal place. The role of ions in electrolysis is emphasized, p. 228, but the equally important part the electron plays fails to receive proper recognition. More exercises are needed to show the student how to use the tables and to appreciate their value. There are no lists of references at the end of chapters to stimulate and guide the ambitious student in further study. This help to both student and teacher will probably be supplied in a practical "Teacher's Manual," which the author has in preparation.

HERMAN SCHLUNDT

Properties of Inorganic Substances. A Second Revision and Enlargement of Tables of Properties of Over Fifteen Hundred Common Inorganic Substances. By WILHELM SÖGERBLÖM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. The Chemical Catalog Company, Inc., 19 East 24th Street, New York, 1927. 226 pp. 23.5 × 16 cm. Price \$6.00.

The purpose of this book, as indicated by the author in the preface to the first edition, is to provide a list of properties of inorganic substances to corroborate tests made in qualitative analysis. The common metallic elements and compounds are grouped in the Fresenius order. Properties are tabulated in parallel columns, facilitating the comparison of thirty-six similar compounds of each of these elements. Thirty-four acids and about sixty less common elements are described in the closing fifty pages of the book.

The present edition is considerably larger than the first edition, and has, apparently, been revised in accordance with data made available during the past two years; about fifty per cent. new material has been

included. Quantitative data on solubilities replace qualitative statements made in the first edition, and a number of new compounds have been added to the tables of elements listed. In the opinion of the reviewer it is unfortunate that the price of the book is somewhat greater than the individual student may care to pay for a supplementary textbook.

There is little doubt that the amount of information a student of one or two year's experience in inorganic chemistry is called upon to acquire very greatly surpasses the amount expected from those who studied chemistry when the general sub-division of the subject, at present in vogue, was instituted. It is a natural result of a study of the needs and abilities of students that teachers are turning more to special aids to memory, such as this book, as a supplement to regular textbooks, and it is the opinion of the reviewer that most of those interested in the successful teaching of chemistry welcome these aids as a means of increasing the usefulness of the student's chemical training and improving his method of study.

While it is possible to list some typographical errors and items of doubtful value in this book, it appears that the general reader will not be helped in evaluating the work by such tabulation. In general, it may be said that the book is relatively free from errors, considering the nature and the wide variety of sources from which the information is necessarily drawn. The reviewer is inclined to approve the publication of such books, and feels that other teachers might well examine the descriptive material given in their courses with a view to rendering it more readily available for students.

C. R. HOOVER

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition, revised System—No 2 **Hydrogen.** Published by the Deutsche Chemische Gesellschaft, Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany; 1927. xxi + 273 pp 3 figs. 18 × 26 cm. Price, to subscribers, 27 M.; singly, 34 M.

This volume follows closely the lines of the earlier instalments. There is first a single paragraph on the history of hydrogen, quite inadequate in itself and equally so in its references to the literature of the subject. There follow excellent sections on the occurrence, formation, preparation and manufacture of hydrogen, totaling 54 pages, and one on its physical properties, occupying 139 pages. Finally, there are sections of about 20 pages each, on the chemical properties of hydrogen, on the two forms of active hydrogen and on the hydrides. Aside from this connected account of the hydrides, the compounds of hydrogen with other elements are not discussed except incidentally, since hydrogen is preceded in the numerical system adopted for this handbook only by the inert gases.

The literature has been covered up to the end of 1926. The collaborators with the Editor in the preparation of this volume were Erich Pietsch, Reinhold Johow, Friedrich Struwe, Heinrich Böttger and Gertrud Wilcke.

ARTHUR B. LAMB

The Problem of Physico-Chemical Periodicity. By E. S. HEDGES AND J. E. MYERS. With a Foreword by Professor F. G. Donnan. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1926. 95 pp. 15 figs. 22.5 × 14.5 cm. Price \$2.75.

The scope of this monograph is indicated by the titles of the chapters: I, Introduction. II, Static Periodicity ("where the periodic property is expressed in terms of some other quantity than time or distance"). III, Periodic Structures (for example, Liesegang rings). IV, Periodic Chemical Reactions. V, The Periodic Catalytic Decomposition of Hydrogen Peroxide. VI, Miscellaneous Periodic Reactions. VII, Periodic Electrochemical Phenomena. VIII, Periodicity and the Metastable State.

There is a Subject Index and a Bibliography arranged as an Author Index. The opinion of the authors that the bibliography is very nearly complete seems well founded.

"The examples of periodic chemical reactions which have been discussed are characterized in the main by heterogeneity of conditions." In the cases considered in Chapters IV and V "periodicity is only realized in the presence of a third constituent," and "the source of the periodicity is in this activating material." It is believed that this material is in a metastable, amorphous form. A close relation to catalysis is evident.

To quote Professor Donnan, "The present work may be warmly commended to the attention of biologists and geologists as well as chemists and physicists."

WILLIAM C. BRAY

Physico-Chemical Geology. By R. H. RASTALL, Sc.D., F.G.S. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1927. vii + 248 pp. 62 figs. 22 × 14.5 cm. Price \$6.00.

This little book is the best of its kind that has come to the attention of the reviewer. It reminds one of the "Principles of Chemical Geology," by J. V. Eidsen. It is not a mere compendium of physico-chemical investigations, like the German texts, but discusses in a practical way selected topics in geology that are helpfully presented in terms of physical chemistry. Several chapters are first introduced on elementary physical chemistry, dealing with equilibrium, change of state, solutions, etc. The petrology that follows is then elucidated in those terms. This part of the subject matter may be indicated by some of the chapter headings: igneous rocks, mineral formation in igneous rocks, metamorphism, rock-weathering,

salt deposits, ore deposits, refractories and colloids in geology. This material has been critically selected and is consequently free from old, discarded or conventional explanations.

Comparatively few references to recent papers and texts are given. For much that is necessarily omitted in a book of this size the reader is referred to United States Geological Survey Bulletin 770, Clarke's Data of Geochemistry. Reference is also made to Boeke's *Grundlagen der phys.-chem. Petrographie*, 1915 edition, but not to the 1923 edition or to Eitel's *physikalisch-chemische Mineralogie und Petrologie*, 1925.

The author adheres to a few chemical terms used more by geologists than by chemists. He also shows a strong preference for British authorities in his references. The geologist should be benefited by the physical chemistry and the physical chemist will find considerable mineralogy, or, more broadly speaking, petrology, in this book. On the whole it is a happy dovetailing of the two fields. The chapter on metamorphism is especially good.

ROGER C. WELLS

Titanium. With Special Reference to the Analysis of Titaniferous Substances. By WILLIAM M. THORNTON, JR., Associate in Chemistry in the Johns Hopkins University. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York City, 1927. 262 pp 26 figs. 15.5 × 23.5 cm. Price \$5 00.

This book is one of the series of monographs prepared under the auspices of the American Chemical Society. It aims to present in compact form all the more important information which has heretofore been presented in dictionaries and in current literature on the subject of titanium.

An introductory section gives in broad outline the circumstances under which the metal was discovered, its occurrence in nature, a general account of the isolation of the metal and the preparation of its important compounds and their industrial applications.

A second section deals with the detection and estimation of titanium in its various associations. The analytical procedure is given in detail for rutile, ilmenite, ferro-titanium, titanium pigment and titanium zinc paint. In other cases the partial procedure is given for the isolation and estimation of titanium alone when associated with other metals. In this analytical section the author has performed a valuable service in collecting and in some cases critically reviewing the large mass of analytical information to be found only in current literature.

The last section gives the methods used by the author in preparing the various reagents with the necessary degree of purity, which are serviceable in the analysis of titaniferous materials.

The book is of special value to the analytical chemist. To the layman the introductory part may give the false impression that titanium plays

a more extensive role in chemical technology than it actually does. As the author states titanium is widely distributed throughout the earth's crust and occurs often in large aggregations from which titanium as oxide is easily extracted. Yet in spite of this it performs but a small function in industry. Its outstanding use is in the preparation of titanium pigments. The alloys of the metal, particularly with iron, have been used as "scavengers" in the past, but this outlet for the material, never very extensive, does not appear to be on the increase. Outside of these two functions the metal is but little used.

It would seem to the reviewer that the research chemist of the future has an important duty to perform in bringing the element titanium into the service of man. To this end Dr. Thornton has taken the first step in bringing all available information into the compass of one volume.

M. A. HUNTER

Colloid Chemistry, Theoretical and Applied, by Selected International Contributors. Collected and edited by JEROME ALEXANDER. Volume I. Theory and Methods. The Chemical Catalog Company, Inc., 19 East 24th Street, New York City, 1926. 974 pp. 324 figs. 16 X 24 cm. Price \$14.50.

This is the first volume of a three volume compendium on colloid chemistry. The sub-title of the first volume is Theory and Method; that of the second, Biology and Medicine; that of the third, Technology.

There are in this volume sixty contributions covering the most diverse branches of chemistry and physics, and for that matter of the other physical sciences. One will find not only papers dealing with the behavior of colloids in biology, geology and meteorology but there are papers even on the colloidal aspects of astronomy!

The list of contributors is remarkably cosmopolitan in character, almost every civilized country in the world being represented. It is also a very distinguished one; it includes five Nobel Prize winners.

The articles in general are not cursory and impromptu notes; they are for the most part well considered and thorough reviews of the particular field of colloid chemistry in which the authors are authorities, frequently accompanied by recent and previously unpublished accounts of new researches.

It is beyond the limits of this book review to list the titles of the sixty contributions. I shall, however, in order to indicate the scope of the collection, arrange the papers in classes and give the names of the authors as follows:

There are seven papers dealing with the general theories of colloids, by Jerome Alexander, P. P. von Weimarn, G. Friedel, E. Buchner, J. W. McBain, E. F. Burton, R. A. Millikan; four on surface energy, surface films, etc., by W. D. Harkins, W. H. Bragg, P. L. du Noüy, R. E. Wilson;

thirteen on processes of aggregation, on optical phenomena, meteorology and the cosmos, by W. E. S. Turner, W. B. Hardy, H. R. Kruyt, Albert Einstein, W. H. Martin, René Audubert, Hsien Wu and Daisy Yen Wu, W. E. Gibbs, Carl Barus, W. J. Humphreys, H. T. Barnes, H. N. Russell, W. D. MacMillan; six on thermal, electric and osmotic effects and on the critical state, by F. L. Browne and J. H. Mathews, Leonor Michaelis, J. Errera, J. Duclaux, Irving Langmuir, W. Kopaczewski; thirteen on various aspects of adsorption, by H. Freundlich, H. B. Weiser, Jerome Alexander, H. Wislicenus, H. J. M. Creighton, G. A. Hulett, J. Traube, T. Hagiwara, S. Utzino, A. Lottermoser, A. de G. Rocasolano, Richard Lorenz, L. L. Bircumshaw; three on viscosity, by E. C. Bingham, W. H. Herschel, Emil Hatschek; six on gels and diffusion, by S. C. Bradford, Dorothy J. Lloyd, R. E. Liesegang, H. N. Holmes, H. A. Endres; and finally eight on apparatus useful in colloid chemistry, by Max Poser, R. Zsigmondy, H. Bechhold, T. Svedberg, E. E. Ayres, Jr., Sven Odén, Henry Bassett.

This collection is a splendid achievement and a real tribute to the energy, enthusiasm and breadth of view of its Editor. Indeed, to have secured so distinguished a body of contributors and to have had them function individually and collectively with such success establishes him as an impresario of the first rank. Finally, his phrase in the Preface that "It is we who are simple, not Nature" deserves perpetuation.

ARTHUR B. LAMB

Enzymes: Properties, Distribution, Methods and Applications. BY SELMAN A. WAKSMAN, Associate Professor of Soil Microbiology, Rutgers University; Microbiologist, New Jersey Agricultural Experiment Station, and WILBURT C. DAVISON, Associate Professor of Pediatrics, Johns Hopkins University; Associate Pediatrician, Johns Hopkins Hospital (more recently, Dean of the School of Medicine, Duke University). The Williams and Wilkins Company, Baltimore, 1926. xii + 364 pages. 11 Figs. 23.5 X 15.5 cm. Price \$5.50.

The purpose of this book is stated by its authors in their preface as follows: "It has been our endeavor to collect in as concise form as possible the available information in regard to enzymes and to indicate the original sources from which more detailed knowledge may be obtained. Anyone who attempts a study of enzymes cannot fail to be struck by the vast accumulation of literature on the subject, while at the same time he will be confused by the many apparently contradictory results that have been published. Over two thousand references have been consulted—most of them in the original—the others in abstracts which have appeared in various journals. To piece these irregular and loosely fitting fragments together into a mosaic upon which future studies may rest is the object of this book." In the judgment of the reviewer, the authors in thus stating their purpose have also offered a word which well characterizes their work;

it is a carefully wrought mosaic rather than a unified thesis or a flowing narrative.

The section entitled "properties of enzymes" occupies 56 pages; "distribution of enzymes," 62 pages; "methods for the preparation and study of enzymes," 131 pages; "practical applications of enzyme activity," 14 pages; bibliography, 78 pages; index, 14 pages.

In view of the professional interests of the authors, as mycologist and physician respectively, it is natural to find that the medical and microbiological aspects of the subject are more fully developed than the technological or the purely chemical. Chemical theories of enzyme action are much less ambitiously treated than by Falk, and many descriptive matters are developed less fully than by Oppenheimer and Kuhn; but Waksman and Davison, defining enzymology as a branch of biology and reviewing with special care and thoroughness some of the more biological aspects, have also presented to the science of chemistry the best effort which the reviewer has yet seen to condense into a single readable volume, a judicial and reasonably symmetrical account of those whole fields of science in which enzymes play a dominant role and to connect effectively their concise text with the original literature of this comprehensive subject. And the chemist, realizing his debt to these authors, does not feel inclined to dwell too heavily upon the occasional loose use of a chemical term, as when zymases are said to "hydrolyze" sugar (p. 244), nor to complain too bitterly at a choice of boundaries which includes less well defined oxidases while omitting glutathione. Dogmatic statements are encountered to a somewhat greater extent than might be anticipated in view of the preface; but the prevailing tone of the book is commendably unbiased throughout, and its breadth of view and careful correlation of readable text with comprehensive bibliography will make it useful both to students of divergent interests who wish general information on enzymes and to special students of the subject who will profit by this introduction to the extensive original literature of both animal and vegetable enzymes, including those of the microorganisms.

Perhaps as an inevitable concomitant of its comprehensiveness, the text sometimes presents a compilation of opinions rather than an attempt to analyze the actual experimental evidence upon a doubtful or disputed point. It is a pity that this should result in a failure to recognize the importance of the excellent work upon the chemical nature of malt amylase which was published by T. B. Osborne in *THIS JOURNAL* over thirty years ago.

H. C. SHERMAN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

COPPER-CONSTANTAN THERMOCOUPLES AND THE HYDROGEN THERMOMETER COMPARED FROM 15 TO 283° ABSOLUTE

By W. F. GIAUQUE, R. M. BUFFINGTON¹ AND W. A. SCHULZE

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One of the most important tasks of a laboratory engaged in low-temperature calorimetric and other measurements is the maintenance of a secondary thermometric standard.

Since 1918, the secondary standard of this Laboratory has been the four-junction copper-constantan thermocouple calibrated between 60 and 300°K. to an accuracy of 0.1° by Eastman and Rodebush.²

This thermocouple has been compared frequently with the freezing point of mercury since the original calibration, and has always been in closer agreement than the stated limits of accuracy.

However, for a number of reasons, the preparation of a new secondary standard has seemed necessary, the chief of these being the extension of the obtainable temperatures by the use of liquid hydrogen.

The gap between 15 and 60°K. has in some cases been bridged by making use of the triple- and boiling-point temperatures of hydrogen, but at best this leads to large uncertainties. For this reason, considerable data have for some time been withheld from publication, pending the conclusion of the work presented in this article.

Most of the recent calorimetric work in this Laboratory has utilized resistance thermometers which can be made much more sensitive and suitable for temperature interpolation than are thermocouples. This is especially true at very low temperatures.

However, at least for the immediate future, copper-constantan thermocouples were again chosen as the reference standard. This was primarily

¹ National Research Fellow in Chemistry, University of California.

² Eastman and Rodebush, *THIS JOURNAL*, 40, 489 (1918).

because they are much more convenient, and also because the experience with the Eastman-Rodebush standard couple had been satisfactory.

The convenience of thermocouples depends largely on the fact that they may, after calibration, be soldered to a metal apparatus, thus insuring excellent thermal contact. Resistance thermometers which may be detached for calibration have sometimes been used, for example, by Keesom and Onnes.³

It is expected that most cryogenic work in this Laboratory will, at least for some time, make direct use of fixed-resistance thermometers which are continuously calibrated during measurements by means of an attached thermocouple. This permits a precision in the measuring of small temperature intervals beyond that possible with a thermo-element alone, and at the same time furnishes a valuable check on the temperature measurements.

The effective portions of a thermocouple are those located in temperature gradients, and it is important that no inhomogeneities of a physical or a chemical nature occur at such places. When possible, tests for the effect of inhomogeneities should be carried out at temperatures approximating those at which the thermocouple is to be used. We believe that the use of liquid air as described is an unusually severe test.

The Thermocouple Wire

The Laboratory supply of constantan, consisting of 58 spools of various sizes and amounts, including 20 spools of No. 30 B. and S. gage, was tested. The e.m.f. against copper between 83 and 273°K. was measured in each case, and in most cases a loop was run through liquid air and galvanometer deflections were noted as a measure of imperfections. Sharp turns were prevented by means of a submerged glass U with a radius of about 6 cm. The warm ends of the loop were attached to copper and kept in an ice-bath. About 1.5 meters of each sample was pulled through, and the procedure was then reversed.

Table I shows typical results on the best constantan wire of various sizes. The deflections in the case of the poorer wire went as high as 10 microvolts, even in the larger sizes. It is evident from the data that very small wire should not be used. The severe gradient imposed by the test would be somewhat greater in the case of small wires, but the same situation might arise in the normal use of thermocouples.

TABLE I
TESTS ON CONSTANTAN WIRE

Size, B. and S. gage	25	30	35	40
E.m.f. vs. Cu at 83°K., microvolts	5468	5810	5791	5609
Av. e.m.f., microvolts	0.24	0.35	0.87	1.84
Maximum	.7	.8	2.0	3.1

³ Keesom and Onnes, *Comm. Phys. Lab. Leiden*, 143, 1914.

Table II shows the e.m.f.'s of some copper-copper thermocouples with junctions at liquid air and ice temperatures in each case. It is evidently necessary to use the same copper for all couples when close agreement is desirable for intercomparisons.

TABLE II
TESTS ON COPPER WIRE

Size	20	24	28	36(a)	36(b)	36(c)	40(a)	40(b)
E.m.f. vs. No. 36(a) junctions								
83 and 273°K., microvolts	+2.7	-0.5	-5.2	(0.0)	-0.2	-0.1	-27.1	+13.8

The Thermocouples

Since it was desired to solder the couples to apparatus, the use of multi-junction couples was eliminated. At the suggestion of Dr. D. H. Andrews, parallel constantan wires were used to average out, partially, small imperfections. This method has recently been used by Hovorka and Rodebush.⁴

Six thermocouples, designated as J, W, 15, 16, 17 and 18, respectively, were made. Each consisted of five No. 30 double-silk-covered constantan wires, and one No. 36 double-silk-covered copper leading to the variable junction. J and W each had five No. 36 copper leads to the individual constantan wires at the ice ends, while 15, 16, 17 and 18 had only one No. 36 copper lead from the ice end in each case. The five No. 30 constantan wires had about the same thermal conductivity as one No. 36 copper wire.

In addition to the above, one couple was made from another spool of No. 30 constantan, which gave 5494 microvolts when opposed to copper at 83 and 0°K. The loop test on this wire gave an average deflection of 0.34 and maximum deflection of 0.9 microvolt. Four parallel constantan wires with separate No. 36 ice ends were used. All of the couples, each of which was 268 cm. long, were wrapped with silk thread.

The Thermocouple Comparison Apparatus

All of the variable junctions were well soldered to a solid cylinder consisting of about 1 kg. of lead. This was suspended within a hollow lead and copper cylinder of about 1.2 kg., which was itself suspended within a brass container suitable for high vacuum.

Each couple was wound twice about the outer cylinder and three times around the inner one, 72 cm. being used in this way as a protection against heat leak into the junctions. The wires wound on the cylinders were heavily paraffined, and the whole was wound with adhesive tape.

Other details of construction and temperature control were quite similar to those of the final gas-thermometer apparatus, and will be described in that connection.

⁴ Hovorka and Rodebush, *THIS JOURNAL*, 47, 1614 (1925).

Table III shows some typical results of the constantan comparison. Col. 1 gives the approximate e.m.f. against copper. Cols. 2-6, inclusive, give the differences between the various parallel groups of constantan wires. Cols. 7-10 show the comparison of the individual constantan wires contained in the parallel group of J. All differences were determined with a galvanometer, using the double-deflection method. The reversing switch was located at the apparatus, thus practically eliminating any error from electrical leaks.

Comparison of the results on single wires and on parallel groups shows that the latter are considerably more reliable, as was to be expected. The algebraic signs are all consistent; thus, when $15\text{-Cu} = 5220.00$ and $J-15 = -0.45$, then $J\text{-Cu} = 5219.55$. Comparisons were made at intervals of about 10° .

TABLE III
TYPICAL RESULTS OF CONSTANTAN COMPARISONS

(Values are given in microvolts)									
15-Cu	J-15	W-15	16-15	17-15	18-15	5-6	5-7	5-8	5-9
6587	-0.63	-0.74	+0.11	+0.48	+0.30	-0.36	-0.42	-0.39	-0.46
6014	-.53	-.63	+.17	+.52	+.32	-.51	-.44	-.44	-.54
5220	-.45	-.54	+.13	+.13	+.52	+.31	-.53	-.26	-.44
3185	-.44	-.36	-.02	+.15	+.06	+.46	+.00	-.37	-.48
- 2	+.02	-.05	-.03	+.03	-.03	+.07	+.09	+.09	+.02

The differences between the various copper wires, as shown in Table IV, were somewhat unexpected, since all of the wire was taken from the same spool (No. 36 a).

TABLE IV
TYPICAL RESULTS OF COPPER COMPARISONS

15-Cu	$W_{Cu}\text{-}J_{Cu}$	$15_{Cu}\text{-}J_{Cu}$	$16_{Cu}\text{-}J_{Cu}$	$17_{Cu}\text{-}J_{Cu}$	$18_{Cu}\text{-}J_{Cu}$
6518	+0.29	+0.76	+0.48	+0.97	+1.40
6336	+.20	+.36	+.27	+.62	+0.92
6014	+.09	+.10	+.10	+.37	+.51
5220	+.01	-.12	-.03	+.14	+.12
3185	-.06	-.20	-.10	-.05	-.10
- 2	-.02	-.04	-.01	-.04	-.02

Thermocouple 17 was selected for comparison with the hydrogen gas thermometer.

The Hydrogen Thermometer

The hydrogen-thermometer comparison apparatus used differs considerably from instruments used for this purpose by others. It was modeled after a calorimeter for the investigation of liquefied and solidified gases used by Giauque and Wiebe for a series of measurements soon to be published.

The apparatus is shown in Fig. 1.

D is a vacuum-tight monel container with connecting tube shown at A. The cover of D was equipped with a cup (not shown) which could be filled with water as a protection for the wires while the cover was being soldered on. B is a 6kg. block of lead. F is a hollow cylinder of lead and copper weighing about 7.5 kg. and supported from the cover of D by stout cords. G is a vacuum-tight 1.5kg. copper and lead container for the thermometer bulb. The spaces between D and F and between F and G could be evacuated. C is a German silver tube leading from G through F and then out at the top of Tube A. The 0.8mm. capillary leading from the 194.3cc. Pyrex bulb, shown at H, was taken out through Tube C. Hydrogen gas could be admitted through Tube C to the space around the capillary and bulb. A rough manometer was used in keeping this pressure approximately equal to that within the bulb, thus eliminating the necessity of pressure correction on the bulb volume. At Position E the tube C was securely soldered to Cylinder F, and the space between the capillary and tube was filled with Rose's metal for a length of 2 cm., with the exception of two very fine thin-walled glass tubes for the passage of hydrogen. Also, the capillary was wrapped at intervals of 2 cm. with narrow strips of adhesive tape until the space between the capillary and Tube C was nearly tight at these points.

The purpose of the adhesive tape and of the Rose's metal was to minimize longitudinal and insure radial conduction. F and G were equipped with electric heaters for temperature control. Control thermocouples were attached to D, F and Tube C at points 20, 40 and 60 cm. above Position E. The temperature at 80 cm. above Position E was taken with a mercury thermometer in a cup attached to a copper case which also enclosed the capillary leading to the manometer. These temperatures were necessary in making the correction for the amount of gas in the capillary.

The top of Tube C was attached to the capillary by means of rubber tubing and de Khotinsky cement to avoid strain by unequal expansion. All wires were taken out through de Khotinsky cement.

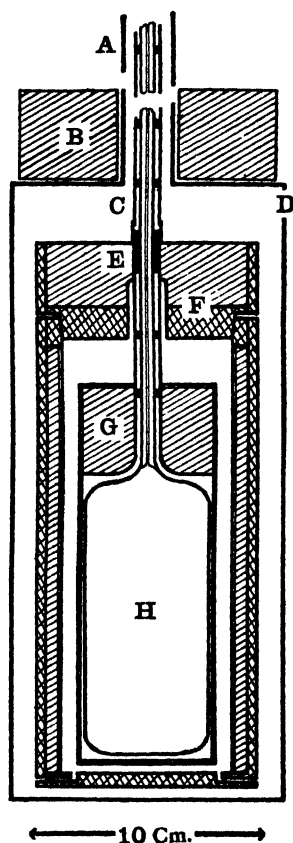


Fig. 1.

Production and Control of Low Temperatures

All temperatures below room temperature were produced by either liquid air or liquid hydrogen at normal or reduced pressures. For example, at temperatures above 100°K., liquid air was used in small quantities, so that no great temperature difference existed between Container D and Cylinder F, Fig. 1. The apparatus was first cooled to the lowest desired temperature, Container D being filled with several centimeters' pressure of hydrogen to supply the necessary conduction. Container D was then evacuated to a pressure of about 10^{-5} mm. of mercury or better. Cylinders F and G were then easily adjusted to equal tempera-

ture by means of their electric heaters. The high vacuum reduced the heat leak to such an extent that the temperature of Cylinder G would not change by 0.01° during the course of a measurement.

Placing of Thermocouple

Thermocouple No. 17 was soldered to the lower portion of container G. It was also otherwise placed as nearly as possible in the same manner as that used in the comparison apparatus. Particular attention was paid to having the temperature gradient occur in the same portion of the wire.

The Manometer

The manometer and auxiliaries are shown in Fig. 2. J and L indicate the arms of the manometer, the inside diameter of each being about

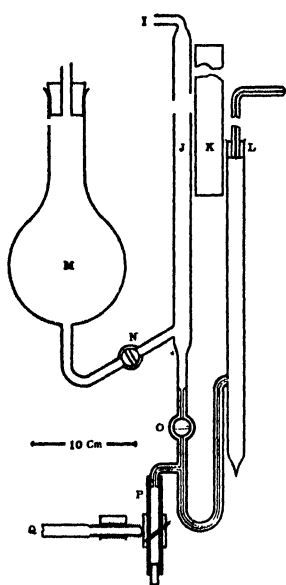


Fig. 2.

1.2 cm. L also indicates a very close-fitting monel plug, carrying the thermometer capillary and cemented in with melted shellac and de Khotsinsky cement. A 0.07cm. tip, which was off center in the line of vision, projected from the lower side of the monel plug as a reference point in adjusting the mercury level in that arm. See the description of the manometer used by Cath and Onnes.⁵ A standard meter is shown at K. M shows the mercury reservoir with central stopcock at N. The capillary shown near O was a partial guard against rapid flow of mercury in case Stopcock O was opened while the manometer was out of balance. P shows a rubber tubing with clamp actuated by a screw worked by a series of reduction pulleys through Shaft Q. This permitted a fine adjustment of the mercury level. Tube I was attached to an evacuating system with mercury-diffusion pump and McLeod gage. The hydrogen was admitted

through Tube I before filling with mercury.

All of the apparatus shown in Fig. 2 was enclosed in a tight wooden case with a plate-glass window. The temperature of the case was controlled by a stream of air from the Laboratory compressed-air system. This gave a temperature which varied very slowly with time. The lighting of the menisci and meter was by means of focusing flashlights and a spotlight, all located far enough away to avoid large heating effects, and was used intermittently. The temperature of the mercury was obtained by means of four mercury thermometers.

⁵ Cath and Onnes, *Comm. Phys. Lab. Leiden*, No. 156a, 1922.

Pressure Measurements

The pressure measurements were made by using a Société Générale cathetometer for the comparison of the mercury menisci with the nearest millimeter ruling on the standard meter. The accuracy was 0.02 mm. The manometer case was tapped before each measurement to prevent sticking of the menisci. Since there was a high vacuum over the mercury in Tube J, direct pressure readings were secured. The correction for meniscus depression was that given in the International Critical Tables.⁶ Since both arms of the manometer were of the same diameter, this correction was nearly balanced out.

Electrical Measurements

Two White double potentiometers were used simultaneously for the electrical measurements, one for the control thermocouples, and one of 10,000 microvolts' range with a galvanometer of low critical ramping resistance for the standard couple. The latter potentiometer was calibrated.

All wiring between the apparatus and potentiometer was supported from the lower side of highly insulating strips of Bakelite, and the whole system electrically shielded.

Temperature Variation of Bulb Volume

The correction for the diminution of bulb volume at low temperatures was made possible by the expansion measurements of Buffington and Latimer⁷ on Pyrex. Their measurements extend only to liquid-air temperatures, thus necessitating considerable extrapolation. Fortunately, however, the nature of the correction is such that it becomes less important at very low temperatures.

The Obnoxious Volume

The obnoxious volume consists of the connecting capillary and the volume between the mercury meniscus and the monel plug. The latter volume was calculable from meniscus data in the International Critical Tables.⁸ Data for this calculation were secured with each measurement.

In making the correction for the amount of gas in that section of the capillary within the temperature gradient, a graphical method was used.

Preparation and Purity of Hydrogen

The preparation of the electrolytic hydrogen was the same as that described by Latimer, Buffington and Hoenshel,⁹ except that the rate of

⁶ International Critical Tables, McGraw-Hill Book Co., New York, 1926, vol. I, p. 70.

⁷ Buffington and Latimer, *THIS JOURNAL*, 48, 2305 (1926).

⁸ Ref. 6, p. 72.

⁹ Latimer, Buffington and Hoenshel, *THIS JOURNAL*, 47, 1571 (1925).

flow over the nickel catalyst used for removing oxygen was 0.1 cu. meter per hour, and an extra tube of nickel catalyst was used as an added precaution. Although hydrogen prepared in the above manner contains less than 0.01% of oxygen, it was still further purified by standing over charcoal at liquid air temperature. The charcoal had previously been heated and pumped with a mercury diffusion pump.

Filling the Thermometer

The thermometer bulb was evacuated with a mercury diffusion pump and swept out with pure hydrogen several times before the final filling. The evacuation was slow because of the small diameter of the capillary. More than a week was required for the above procedure.

Reconstruction of Apparatus

After the completion of runs referred to as 1 and 2, one of the supports of the heavy cylinder gave way, and the capillary leading to the manometer snapped off. Also, after removal, thermocouple No. 17 proved to have developed a short circuit. The apparatus was repaired and Thermocouple J was used instead of immediately repairing No. 17. The silk insulation of 17 was easily repaired later. The bulb was refilled with hydrogen, and runs designated as 3, 4 and 5 were made. The reconstructed apparatus and new thermocouple proved to be a valuable check on the previous measurements.

The Ice Point

It was realized in the designing of the apparatus that the thermometer bulb could not be brought with sufficient accuracy to the ice point by surrounding the whole apparatus with ice; in fact, this experiment was not tried. However, it has been shown that the maximum difference in e.m.f. between any of the couples when the variable junctions were at the ice point was 0.07 microvolts, corresponding to 0.002°. This

TABLE V
ICE-POINT PRESSURES

	Press., cm.	Valued used, cm.
Immediately after filling	97.916	
Before Run 1	97.924	
		97.926
End of Run 1	97.926	
End of Run 2	97.933	
	97.938	97.935
After refilling for Runs 3, 4 and 5	96.791	
	96.787 ^a	
	96.783	96.783
Near end of Run 5	96.782	

^a Heavy protective cylinder cooling rapidly.

enabled the ice point to be obtained by adjusting the temperature of the heavy cylinders until the thermocouple reading was zero, or nearly so. Table V shows the ice-point data.

The ice-point pressure gradually increased during Runs 1 and 2. The apparatus was known to be tight at the start by test with a McLeod gage before filling, but considerable difficulty was encountered in displacing the hydrogen by mercury in Tube P, Fig. 2, and small bubbles were observed on several occasions in the adjoining tube. The gas eventually rose into Tube J and was pumped off, but some apparently was carried into Tube L, Fig. 2, on the few occasions when the mercury moved rapidly through the capillary U. There is also some possibility that the plug in the bottom of Tube P leaked slightly, which might admit some air. If the gas were hydrogen it would make no difference as to the results, while even if it were air the effect would not exceed 0.01° in the most unfavorable case.

Before Runs 3, 4 and 5, Tube P was renewed and filled with mercury before hydrogen was admitted. The pressure then showed a slight decrease with time. The result marked *a* was obtained after rapidly heating the bulb from the neighborhood of liquid-air temperatures, and may indicate some temperature lag in bulb volume as well as the effect of other unfavorable conditions.

Most of the measurements were made by four observers simultaneously recording the various data.

Treatment of Results

The data were treated as follows. An approximate temperature scale (accurate to a few tenths of a degree) was calculated. The various corrections could then be applied, giving a table of e.m.f. and temperatures on the hydrogen scale. The data of Cath and Onnes⁵ were used for correcting the temperatures from the hydrogen to the thermodynamic scale.

A plot of $\Delta\epsilon/\Delta T$ against T was constructed. Approximate $d\epsilon/dT$ and ϵ values were chosen. First and second differences of the $d\epsilon/dT$ values were tabulated. The approximate table was used to calculate the individual points. Guided by the above comparison, the $d\epsilon/dT$ differences were smoothed, and the final Table VI was constructed for Thermocouple 17. Fig. 3 shows the comparison of the temperatures given by the gas thermometer with those calculated from the thermocouple readings by means of Table VI. No absolute significance is to be attached to the data in Table VI, but it should prove useful in the construction of deviation plots for interpolating data of other thermocouples when only a few points are available. This is the method suggested by Adams,¹⁰ but his data extend only to liquid-air temperatures. An

¹⁰ Ref. 6, p. 57.

equation method could be used, but aside from the considerable difficulty in obtaining an equation to fit the observed data, we believe the deviation plot to be the more advantageous method.

TABLE VI
TEMPERATURE CONVERSION TABLE

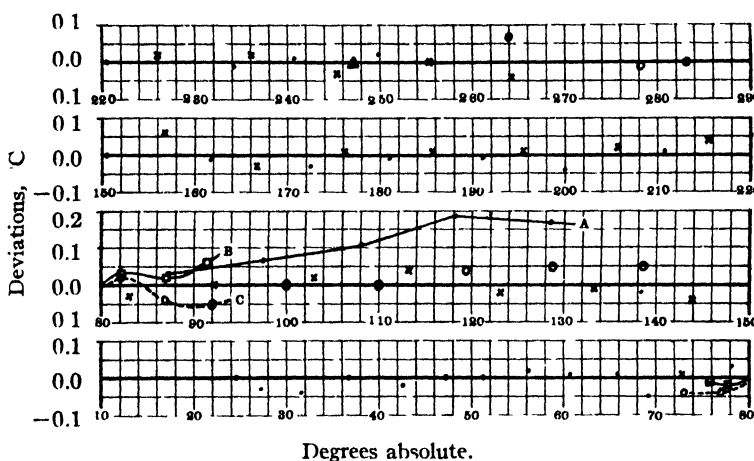
$T, ^\circ\text{K.}$	d_s/dT	Diff.	$T, ^\circ\text{K.}$	d_s/dT	Diff.
25	6586.0		160	3996.9	
		39.1			293.0
30	6546.9		170	3703.9	
		45.6			305.5
35	6501.3		180	3398.4	
		51.7			317.9
40	6449.6		190	3080.5	
		119.1			330.0
50	6330.5		200	2750.5	
		138.2			341.9
60	6192.3		210	2408.6	
		155.3			353.3
70	6037.0		220	2055.3	
		171.0			364.5
80	5866.0		230	1690.8	
		185.5			375.2
90	5680.5		240	1315.6	
		199.6			385.7
100	5480.9		250	929.9	
		213.6			396.0
110	5267.3		260	533.9	
		227.3			406.0
120	5040.0		270	127.9	
		241.0			415.7
130	4799.0		280	-287.8	
		254.3			425.2
140	4544.7		290	(-713.0)	
		267.4			(42.99)
150	4277.3				
		280.4			

Since the completion of the work considered in this paper, Giaque, Johnston and Kelley have made a comparison of the scale here obtained with the hydrogen and oxygen vapor-pressure thermometers. This work, which is described in a following paper,¹¹ shows that the measurements below 25°K. are in error, presumably due to adsorption of hydrogen within the thermometer. We have accordingly extended Table VI only to 25°K. The extension of Table VI to 13°K., as well as a discussion of the adsorption effect, will be found in another paper.¹¹

The results between 87 and 128°K. in Run 2 show the effect of neglect with regard to the ice junction. The ice had been in use for nearly 20

¹¹ Giaque, Johnston and Kelley, *THIS JOURNAL*, **49**, 2367 (1927).

hours when this effect took place. The result at 264°K . in Run 5, which deviates by 0.07° , was taken after rapid warming from 138°K . and may indicate lag in the Pyrex bulb. The ice point immediately following this measurement was also off in the same direction. The greatest lack of agreement seems to be in the range where the obnoxious volume correction is most important, that is, at about 140°K . The effect of having the temperature gradient larger or smaller than was normal for the apparatus as used seems to be quite definite. It is difficult to segregate the effect on the gas thermometer from that on the thermocouple, but we suspect the latter. To our knowledge there is no theoretical or experimental reason to suppose that the irreversible heat flow which is necessarily



× Run 1. • Run 2. Δ Run 3. □ Run 4. ○ Run 5. A, new ice on junction; B, temperature gradient large as possible, C, temperature gradient small as possible

Fig. 3.—Deviation graph.

present in thermocouples may not be contributing appreciably to the e.m.f., and if so the amount due to this factor may depend on the character of the gradient. The effect referred to is of course not to be confused with those due to inhomogeneity. However, regardless of the nature of the small disturbances always observed in the use of thermocouples, it is obviously desirable to calibrate thermocouples under conditions nearly the same as those which exist when they are used.

The agreement of results with Thermocouples 17 and J was satisfactory. All of the results with J are expressed in terms of No. 17.

In connection with other experimental work, as yet unpublished, initial comparison with the temperature scales of others is available. Giauque and Wiebe have measured the vapor pressure of hydrogen chloride, using Thermocouple 18 as a reference standard. The results agree with those

of Henning and Stock¹² to one or two hundredths of a degree. This agreement is particularly significant since the work of Henning and Stock in the *Physikalisch-Technischen Reichsanstalt* was for the purpose of establishing thermometric standards. Their hydrogen chloride data extend from 156 to 186°K.

Before the hydrogen thermometer measurements were made, the e.m.f. of Thermocouple 17 in melting mercury had been measured. From Table VI this e.m.f. corresponds to a temperature of 234.18°K. The value given in the International Critical Tables is 234.23°K. The agreement is satisfactory, especially considering that the temperature gradient in this case was not in the same portion of the wire in which it occurred during the calibration. Other investigations in progress in this Laboratory will provide still other comparisons.

The results above 25°K. are believed to be accurate to 0.05°, which is considered quite satisfactory for present requirements.

The research described in this paper has been regarded as of a laboratory rather than an individual nature, and many besides the co-authors have contributed. We wish to express our thanks to W. M. Latimer, D. H. Andrews, H. D. Hoenshel, S. S. Shaffer, and particularly to R. Wiebe and H. L. Johnston, who assisted in making Runs 1 and 2.

Summary

The testing of constantan and copper wires for thermocouple use at low temperatures has been described.

The comparison of copper-constantan thermocouples with each other and with the hydrogen gas thermometer from 15 to 283°K. has been carried out, and considerable information is given as to what may be expected of carefully prepared thermocouples over the above range.

A gas thermometer has been described with which it is easily possible to obtain and maintain to 0.01°, for sufficient time, any temperature from that of liquid hydrogen to room temperature.

A table showing the properties of a typical copper-constantan thermocouple from 25 to 283°K. is included.

BERKELEY, CALIFORNIA

¹² Henning and Stock, *Z. Physik*, **4**, 226 (1921).

THE REACTION OF SODIUM CHLORIDE IF ADDED TO A SOLUTION OF LITMUS AND MERCURIC CHLORIDE¹

By WILLIAM OVID MOOR

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It has been known for many decades that an aqueous solution containing either equivalent amounts of mercuric chloride and sodium chloride or sodium chloride in excess, does not change the color of blue or violet litmus, whereas a solution of corrosive sublimate alone has an acid reaction. I was indeed able to convince myself that red, violet or blue litmus did not react in any way with a solution containing mercuric chloride and sodium chloride, if the latter was present in an equivalent proportion or in excess to mercuric chloride.

This phenomenon has been explained on the ground that chloride of sodium and bichloride of mercury form a double salt, $\text{HgCl}_2 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$, the reaction of which is neutral. For this reason further study and experimentation will be required to find an adequate explanation for the reaction to be described in the following.

It has been of great convenience to me in the course of my researches that I found a method which enabled me to obtain, whenever needed, a standard violet solution of litmus. By dissolving in a diluted solution of blue litmus some sulfate of zinc, we obtain a liquid which has exactly the same violet color as the best neutral tincture of litmus (for example, Kahlbaum's of the same dilution).² If the blue solution of litmus is not too concentrated, and if the sulfate of zinc has not been used too much in excess, no precipitate will form. By recurring to this method it will be made possible for every laboratory to use neutral solutions of litmus, possessing exactly the same shade of color.

In order to carry out successfully the reaction which forms the subject-matter of this communication, the following requisites should be kept ready on hand:

1. Two test-tubes of small caliber (about 1 cm. in diameter), each containing about 5 cc. of water.
2. A saturated solution (15–20°) of chloride of sodium.
3. A small measuring cylinder containing about 1.25 cc. of this saturated sodium chloride solution.
4. A filtered solution of 2 g. of blue litmus in 30 cc. of water. It is advisable to dissolve the litmus in warm water (50°).
5. Crystallized sulfate of zinc.
6. A solution of 1 drop of concd. hydrochloric acid in 40 cc. of water.

¹ From a paper read before the Chemical Society of Leningrad, on March 4 and April 1, 1926.

² I do not know whether this fact is known to chemists or not.

7. A 2% aqueous solution of bichloride of mercury.
8. Neutral violet litmus paper of the best sort.

Care must be taken that the chloride of sodium which is used here should be of absolutely neutral reaction, so that its saturated solution does not change the color of neutral litmus paper one way or the other. It sometimes happens that even "pure" sodium chloride shows a slightly alkaline reaction if tested with violet litmus paper. In such cases a saturated solution of the salt must be mixed, drop by drop, with a solution of one drop of hydrochloric acid in 40 cc. of water until sensitive neutral litmus paper, when moistened with the liquid, does not assume a tint of blue.

The reaction itself is carried out in the following manner. Five cc. of water is mixed first with 1-2 drops of the blue litmus solution, and then with some crystallized sulfate of zinc. We thus obtain a standard violet solution of litmus. Now we add to another 5 cc. of the diluted blue litmus solution, drop by drop, the above-mentioned solution of one drop of hydrochloric acid in 40 cc. of water, until the two liquids possess exactly the same color. The second 5 cc. of the neutral violet litmus solution is now mixed with 4-5 drops of a 2% aqueous solution of bichloride of mercury, whereupon the mixture at once becomes reddish. On quickly adding to this reddish liquid about 1 cc. of a saturated sodium chloride solution, the mixture, against all expectation, does not assume its original violet color, *but turns blue*.³

For properly estimating the shades of color of these various liquids it is necessary to use test-tubes of a small caliber and to hold them above the level of the eyes, so that the sky shines through the liquid. It need hardly be mentioned that this reaction must be carried out by daylight, the use of artificial light being very misleading.

Supplementary Note on the Reaction of Sodium Chloride with a Solution of Litmus and Mercuric Chloride.—Using the same quantities of the two solutions, sodium chloride and mercuric chloride, as in the original experiment, it makes no difference whether the mercuric chloride is added to the sodium chloride, or the sodium chloride to the mercuric chloride, as long as the litmus is added *last*. In both cases the solutions exhibit a neutral reaction.

If the original experiment is modified by varying the time allowed for the interaction of litmus and mercuric chloride from nearly zero minutes to several hours, the solution, on adding sodium chloride in excess, turns just as blue as in the original reaction. Even when the liquid containing litmus and five drops of the 2% solution of mercuric chloride was boiled for a few seconds the characteristic blue reaction with sodium chloride did not fail to take place.

³ After a few seconds the liquid gradually turns violet.

Only the best kind of litmus should be used, a diluted solution of which has a genuine blue color. It must be mentioned that the degree of blue produced by the sodium chloride is a shade less intense than that produced by adding potassium hydroxide to a neutral violet solution of litmus.

An adequate explanation of the *modus operandi* of the reaction between sodium chloride and litmus + mercuric chloride must account for the following facts.

1. The reaction takes place only if *first* the mercuric chloride has come in contact with the litmus.

2. The blue color produced by the sodium chloride is not lasting; in a few minutes the liquid assumes a violet color.

3. The blue color of the reaction is a shade less deep than the one produced by potassium hydroxide; the solution possesses a tint of lilac, which is not noticed if potassium hydroxide is used instead of sodium chloride.

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WILLIAM OVID MOOR

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, No. 145]

THE CRYSTAL STRUCTURES OF MERCURIC AND MERCUROUS IODIDES

BY MAURICE L. HUGGINS AND PAUL L. MAGILL

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Introduction

Since the determinations of the crystal structures of the mercury iodides here described were completed (in the summer of 1925) other investigators, as shown below, have published x-ray analyses of these substances, their conclusions being substantially in accord with our own. It seems desirable, nevertheless, to publish in brief form our measurements and deductions as they afford an independent confirmation of the results obtained, as our methods of obtaining and utilizing the data differ from those employed by the others, and as our structure determinations are more nearly unique.

This research was carried on while the senior author was a National Research Fellow at the California Institute of Technology. Some of the apparatus used was bought with the aid of a grant to Dr. A. A. Noyes from the Carnegie Institution of Washington. We wish to express our thanks for this aid and also to thank Dr. R. G. Dickinson for the use of apparatus designed by him and for personal instruction in methods of crystal-structure analysis.

A. MERCURIC IODIDE

The red modification of mercuric iodide, HgI_2 , is said¹ to crystallize with ditetragonal bipyramidal (D_4^h) symmetry. The axial ratio¹ (c/a) has been determined as 2.008 and the density² as 6.283 g./cc. The crystals exhibit very perfect cleavage parallel to the (001) faces.

Determination of the Structure from Spectral Photographs Alone

Spectral photographs were obtained, using the Mo K radiation with (1) the c axis, (2) the crystallographers' a axis, and (3) the other possible a axis (making an angle of 45° with that chosen by the crystallographers), as the axis of rotation. All of the reflections observed (from 48 different forms) could be given integral indices on the basis of a unit having the dimensions $a_0 = 4.34 \text{ \AA.}$ and $c_0 = 12.34 \text{ \AA.}$, but not on the basis of any smaller unit. Larger units would leave many unaccounted for absences. These exact values were obtained by direct comparison of the (110) and (001) reflections with those from a cleavage face of calcite.

A unit of this size contains two Hg and four I atoms, the calculated density being 6.45 g./cc. The axial ratio is 2.84, which is just $\sqrt{2}$ times the crystallographers' value. The factor $\sqrt{2}$ arises from the fact that the

TABLE I
DATA FROM SPECTRAL PHOTOGRAPH HgI_2 -4

Form	Rel. inter-planar dist.	Obs. intens.	Rel. intens. calcd. for equal inter-planar dist.	Form	Rel. inter-planar dist.	Obs. intens.	Rel. intens. calcd. for equal inter-planar dist.
Left side of photograph				Right side of photograph			
011	0.944	m	0.185	123	.404	f	.185
012	.818	ms	.313	124	.378	0	.044
013	.686	m	.185	220	.353	ms	1.000
014	.580	vf	.044	125	.352	vf	.185
020	.500	ms	1.000	222	.343	vf	.105
015	.495	f	.185	126	.325	f	.231
022	.472	vf	.105	224	.317	0	.010
121	.442	f	.185	130	.316	0	.020
016	.428	f	.231	132	.309	vf	.288
122	.427	f	.313	127	.301	vf	.185
017	.376	vf	.185	134	.289	f	.992
026	.344	f	.541	226	.283	f	.541
028	.290	f	.714	128	.278	vf	.152
Right side of photograph				231	.276	vf	.185
110	0.707	0	.020	232	.272	f	.313
112	.633	m	.288	233	.266	vf	.185
114	.502	m	.922	234	.258	0	.044
121	.442	mf	.185	235	.249	vf	.185
122	.427	mf	.313	236	.239	vf	.231

¹ Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Vol. 1, p. 218.

² International Critical Tables, Vol. 1.

a axes of the true (namely, the smallest) unit make 45° angles with the a axes chosen by the crystallographers.

The considerations leading to the determination of the arrangement of atoms within the unit are as follows.

1. In each of the spectral photographs the half above the horizontal zone was an exact mirror image of that below this zone.

2. The "special positions" of the correct space group must include either two single non-equivalent positions or a pair of equivalent positions, for the mercury atoms.³

3. The reflections obtained included some from planes of each of the following classes: $(h + k + l)$ odd. $h = 0$; k odd. $h = 0$; l odd. $h = 0$; $(k + l)$ odd. $(h + k)$ odd.⁴

4. All odd order reflections from the (001) planes were absent, although even orders through (008) were obtained. Similarly, odd orders of (010) were absent, although in proper position for reflection.

5. The (110) reflection was absent or extremely weak on photographs showing moderately strong (220) reflections. Moreover, (004) reflections were absent or very faint on photographs showing fairly strong (006) reflections.

6. Certain structures would place the Hg atoms in layers 6.17 Å. apart, with the I atoms either all crowded together in the same planes as the Hg atoms or distributed between alternate layers of Hg atoms, the distance between Hg layers separated by I atoms being the same as between Hg layers having nothing between them. Such structures obviously could not be correct.

Only one tetragonal structure satisfies the requirements imposed by the above considerations. In that, which may be derived from either of the space groups V_d^4 , D_4^0 , or D_{4h}^{15} , the Hg atoms are at the positions (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the I atoms at $(0, \frac{1}{2}, u)$, $(\frac{1}{2}, 0, \bar{u})$, $(\frac{1}{2}, 0, \frac{1}{2} - u)$ and $(0, \frac{1}{2}, u + \frac{1}{2})$.

To determine the value of the parameter u it is necessary to use further intensity comparisons. Great care must be exercised in making use of such comparisons from rotation spectra, since the relative intensities of two spots on the photographic plate depend on a number of other factors besides the relative reflecting powers of the two sets of planes being compared. It would seem safe, however, to use comparisons between spots which are fairly close together on the plate and which differ considerably in intensity, provided the stronger reflection is that further

³ The "equivalent positions" of the various space groups have been tabulated by Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Pub. No. 318 (1922).

⁴ Absences to be expected from the various structures have been tabulated by Astbury and Yardley, *Trans. Roy. Soc. (London)*, 224A, 221 (1924).

from the spot produced by the direct beam. A number of such comparisons are listed in Table II.

TABLE II
COMPARISONS FROM HgI₂-4

012 > 011. 015, 016, 017, 020, 026, 028 > 014. 026, 028 > 017. 026, 028 > 022, 024. 112, 114, 121, 122, 123, 125, 126, 127, 128, 220, 222, 226, 231, 232, 233, 234, 236, 132, 134 > 110. 220 > 112. 220 > 121, 122, 123. 125, 126, 127, 128, 226, 231, 232, 233 > 124. 226 > 125, 126, 127. 132, 134, 231, 232, 233, 235, 236 > 130. 134 > 132. 134, 226, 231, 232, 233, 235, 236 > 224. 232 > 231. 235, 236 > 234.

OTHER COMPARISONS (FROM OTHER SPECTRAL PHOTOGRAPHS)

012, 013, 026, 028, 015, 016 > 002. 006, 008, 013, 015, 016, 017, 018, 019, 026, 028 > 004. 020 > 011. 018, 019 > 014. 028 > 019.

On calculating and plotting the structure factors in the usual manner, it has been found that these comparisons are all satisfied only for the parameter range from $u = .131$ to $u = .150$, if the Hg and I atoms scatter in proportion to their atomic numbers, for a slightly smaller range if the ratio, Hg/I , of their scattering powers is somewhat less than that of their atomic numbers, and for a slightly larger range if the scattering power ratio is somewhat greater than the atomic number ratio. The relative intensities calculated for the planes listed in Table I, assuming $u = .140$ and that the reflecting powers are proportional to the atomic numbers and not correcting for different interplanar distances, are given in the last column of that table.

Corroboration of the Structure with the Aid of Laue Photographs

This structure determination was checked by means of Laue photographs, the analysis being made in the usual way.

TABLE III
USEFUL DATA AND COMPARISONS FROM LAUE PHOTOGRAPH HgI₂-11

Indices	Est. intens.	Interpl. dist., Å.	Wave length, Å.	Indices	Est. intens.	Interpl. dist., Å.	Wave length, Å.
109	3.5	1.31	0.43	2,1,10	1.3	1.04	0.45
0,1,10	0.8	1.19	.33	0,1,12	1.6	1.00	.42
234	.3	1.12	.36	1,0,12	2.0	1.00	.43
234	.4	1.12	.45	1,1,16	0.2	0.75	.44
1,0,11	.4	1.09	.28	2,1,16	.4	.72	.44
235	1.3	1.06	.42	258	.05	.71	.46
325	1.6	1.08	.43	5,2,11	.1	.65	.46
1,2,10	1.3	1.04	.44				

Comparisons: 235 > 234. 0,1,12 > 235. 1,2,16 > 1,1,16. 1,2,10 > 234. 0,1,12 > 1,2,10. 2,5,11 > 258.

By means of intensity comparisons between planes reflecting the same wave length, it was found possible to limit the parameter to quite a small range, namely, between .136 and .142 if we assume reflecting powers

proportional to the atomic numbers, between .138 and .142 if we assume the ratio ($\overline{\text{Hg}}/\overline{\text{I}}$) of reflecting powers to be 10% greater than that of their atomic numbers, and between .136 and .140 if we take $\overline{\text{Hg}}/\overline{\text{I}}$ as 10% less than the atomic number ratio. The uneliminated region disappears entirely if the ratio of scattering powers is assumed to be 22% greater or 28% less than that of the atomic numbers. In view of these results we believe $u = .140 \pm .003$ to be a conservative estimate of the parameter.

Comparison with the Results of Other Investigators

Havighurst,⁵ using powder photographs and ionization spectrometer measurements from single crystal faces, has determined the dimensions of the unit cell as $a_0 = 4.356 \text{ \AA.}$ and $c_0 = 12.34 \text{ \AA.}$ Bijvoet, Claassen and Karssen,⁶ using powder photographs and rotation spectra, have obtained $a_0 = 4.38 \text{ \AA.}$ and $c_0 = 12.43 \text{ \AA.}$ and deduced the same type of arrangement as have we, with $u = .139 \pm .007$.

Description and Discussion of the Structure

The structure (Figs. 1 and 2) may be described as consisting of "layer molecules." The smallest interatomic distance (Hg-I) within each layer, taking u as .140, is 2.77 \AA. ; the shortest distance between atoms (I-I) in different layers is 4.10 \AA. Within each layer each Hg atom is surrounded tetrahedrally by four equidistant I atoms and each I by two

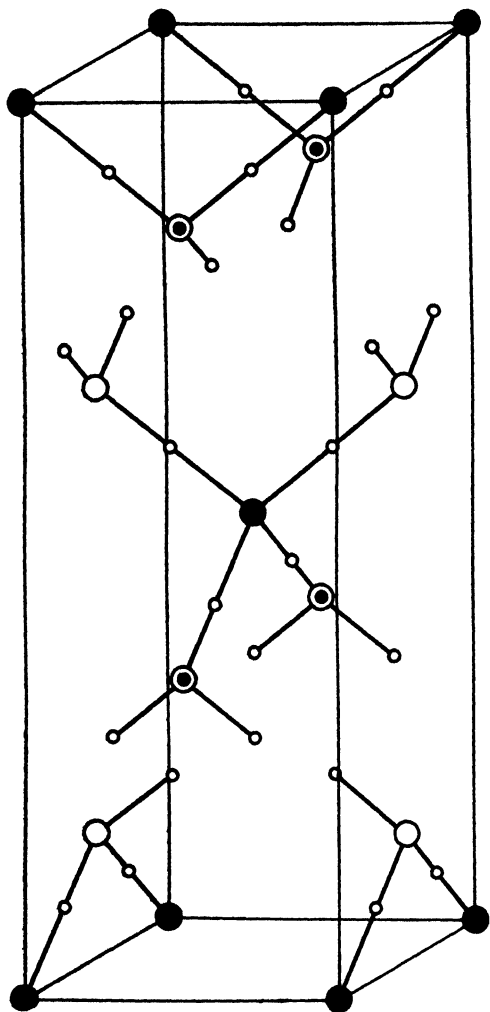


Fig. 1.—The unit cell of HgI_2 . Large dots represent Hg centers and large circles and circled dots I centers. Small circles show the probable approximate "positions" of pairs of valence electrons.

⁵ Havighurst, *Am. J. Sci.*, **10**, 556 (1925).

⁶ Bijvoet, Claassen and Karssen, *Proc. Acad. Sci. Amsterdam*, **29**, 529 (1926).

equidistant Hg atoms. These atoms we may assume to be held tightly together, while the forces between the layers are, relatively weak accounting for the fact that these crystals cleave so readily parallel to their (001) faces.

The most probable distribution of valence electrons⁷ would seem to be that shown in the figures, both Hg and I kernels being tetrahedrally surrounded by electron pairs.

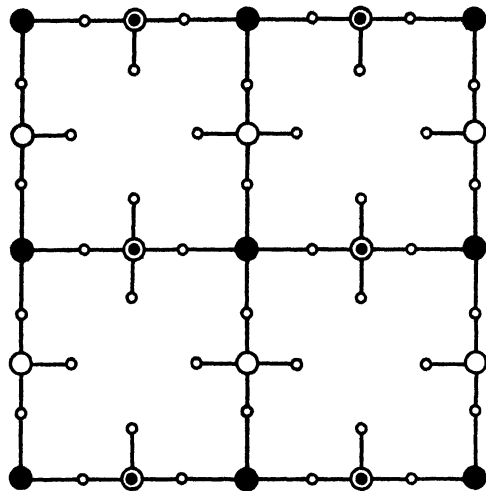


Fig 2.-A small section of a layer in a crystal of HgI_2 .

Assuming such a distribution and defining an atomic radius as the distance from nucleus to the center of a valence pair, it is evident that the distance between Hg and I centers equals the sum of their radii.

One of the authors⁸ has calculated the Hg and I radii, in crystals such as HgS , CuI and AgI , to be about 1.50 Å. and 1.25 Å., respectively. The sum of these values (2.75 Å.) is closer to the observed Hg-I distance (2.77 Å.) than might have been expected, considering

the inaccuracies of the calculations and the differences between the crystals involved.

B. MERCUROUS IODIDE

Crystals of mercurous iodide, Hg_2I_2 , are also tetragonal, with an axial ratio of 1.673 and a density of 7.70 g./cc. Cleavage again is parallel to the (001) planes.

Determination of the Structure

The unit cell found to be in agreement with both the Laue and spectrum data contains four Hg and four I atoms, a_0 and c_0 being 4.92 Å. and 11.64 Å., respectively. The a_0 value was obtained by direct comparison of a (110) reflection spectrum with that from a calcite cleavage face; c_0 was calculated from a_0 , assuming the axial ratio given above to be correct (except for the factor $\sqrt{2}$). This c_0 value was checked approximately

⁷ Cf. Huggins, *Phys. Rev.*, 27, 286 (1926).

⁸ Huggins, *ibid.*, 28, 1086 (1926). New and better data not then available (especially Barth and Lunde, *Norsk geol. tids.*, 8, 281 (1925) and Zachariasen, *ibid.*, 8, 302 (1925)) result in values for some of the radii which differ somewhat from those published. The newer values are used here.

by means of transmission spectra from the (001) planes. The calculated density is 7.68 g./cc.

In determining the type of arrangement within the unit the following observations were found useful:

1. Both spectrum and Laue photographs were symmetrical about lines passing through the central spot.
2. No $(h + k + l)$ odd reflections appeared.
3. Reflections were observed from planes of the following classes: $h = 0$; k odd; l odd. $h = \pm k$; $(2h + l)/4$ not integral. h odd; k odd; $l/4$ integral.
4. $l = 3$ reflections were all absent or extremely weak.
5. $l = 2$ and $l = 6$ reflections were all absent or too faint to be observed.
6. The reflection from (130) was stronger than that from (121).

Applying these data to all tetragonal structures and considering $\overline{\text{Hg}}/\overline{\text{I}}$

TABLE IV
DATA FROM SPECTRAL PHOTOGRAPH Hg_2I_2 -5

Form	Rel. inter-planar dist.	Obs. intens.	Form	Rel. inter-planar dist.	Obs. intens.
Left side of photograph			Right side of photograph		
110	0.707	vs	011	0.922	mf
112	.607	0	013	.619	vf
114	.454	s	020	.500	ms
121	.439	f	022	.460	0
123	.389	0	121	.439	f
220	.354	ms	015	.428	ms
116	.344	0	024	.382	ms
222	.339	0	031	.330	vf
125	.325	m	017	.320	mf
017	.320	mf	130	.316	m
224	.303	m	026	.309	0
130	.316	m	033	.307	0
133	.293	0	132	.305	0
134	.279	mf	134	.279	mf
231	.276	vf	118	.273	m
118	.273	m	035	.273	mf
127	.270	vf	028	.255	mf
233	.262	0	040	.250	mf
235	.239	mf	042	.244	0
330	.236	mf	044	.230	mf
332	.231	0	145	.216	vf
240	.224	mf			
228	.227	f			
242	.220	0			
334	.219	mf			
244	.209	f			

Comparisons: $l = 0 > l = 1, 2, 3$. $1 > 2, 3$. $4 > 1, 2, 3, 6$. $5 > 1, 2, 3, 6$. $7 > 2, 3, 6$. $8 > 1, 2, 3, 6$.

for all values from 1.00 to 2.00, all but the following have been definitely ruled out:

1. C_{4v}^9 (aa,aa). Hg at $(0,0,0)(\frac{1}{2},\frac{1}{2},\frac{1}{2})(0,0,u)(\frac{1}{2},\frac{1}{2},u + \frac{1}{2})$. I at $(0,0,r)(\frac{1}{2},\frac{1}{2},v + \frac{1}{2})(0,0,w)(\frac{1}{2},\frac{1}{2},w + \frac{1}{2})$.

2. (e,e) of V_d^9 , V_d^{11} , D_4^9 or D_{4h}^{17} ; (f,f) of V_d^9 . Hg at $(0,0,u)(0,0,\bar{u})(\frac{1}{2},\frac{1}{2},u + \frac{1}{2})(\frac{1}{2},\frac{1}{2},\frac{1}{2} - u)$; I at $(0,0,v)(0,0,\bar{v})(\frac{1}{2},\frac{1}{2},v + \frac{1}{2})(\frac{1}{2},\frac{1}{2},\frac{1}{2} - v)$. The second is a special case of the first, obtained by putting $w = u - v$ and shifting the origin.

The C_{4v}^9 structure cannot conclusively be eliminated without very tedious calculations. These we have not made, as they seemed unnecessary in view of the satisfactory agreement obtained otherwise and the absence of any crystallographic or other evidence of polarity.

Calculating structure factors for arrangement (2) for various values of l , u , v and $\overline{\text{Hg}}/\bar{I}$, the best agreement with our data (Tables IV and V) was obtained for $u = .117$ and $v = .353$, with $\overline{\text{Hg}}/\bar{I} = 1.3$ times the ratio

TABLE V
SELECTED DATA FROM LAUE PHOTOGRAPHS

Indices	Est. intens.	Interpl. dist., Å	Wave length, Å	Indices	Est. intens.	Interpl. dist., Å	Wave length, Å
Hg ₂ I ₂ -12				Hg ₂ I ₂ -4			
138	0.6	1.06	0.30	$\bar{2}33$	0.2	1.29	0.41
$2, \bar{1}, 11$.6	0.95	.39	$\bar{3}27$.4	1.05	.43
$3\bar{3}8$.2	.91	.30	$2\bar{3}7$.4	1.05	.45
$1, 0, \bar{1}3$	1.6	.88	.30	$\bar{2}, 1, 11$.4	0.95	.41
$3, \bar{2}, 11$	0.2	.84	.39	$1, \bar{2}, 11$.4	.95	.42
$\bar{3}, 2, 11$.2	.84	.44	$5\bar{3}0$.6	.84	.40
$1, 1, 14$.5	.81	.33	350	.6	.84	.42
$1, 1, \bar{1}4$	1.0	.81	.39	$1, 2, 13$	3.5	.83	.45
$4\bar{3}9$	0.6	.78	.43	$2, 1, 13$	3.5	.83	.44
$1, 2, 15$.1	.73	.38	534	.4	.81	.41
$1, 2, \bar{1}5$.05	.73	.43	Hg ₂ I ₂ -1			
$1, 1, \bar{1}6$.1	.71	.30				
$4, \bar{3}, 13$.1	.66	.30	$3\bar{2}3$	0.05	1.29	0.42
$4, 3, 13$.1	.66	.34	$4, \bar{1}, 13$.4	.72	.42
549	.1	.66	.37	529	.1	.67	.41
$\bar{5}49$.1	.66	.39				
$1, 3, 16$.05	.66	.40				
$1, 2, 17$.2	.65	.30				
$1, 2, \bar{1}7$.4	.65	.35				
$2, 1, \bar{1}7$.4	.65	.41				
$1, 4, 17$.2	.59	.40				
$\bar{4}, 1, 17$.1	.59	.43				
$4, \bar{1}, 17$.2	.59	.39				

No $l = 2, 6$ or 10 reflections in first order on any of above photographs.

Comparisons from Hg₂I₂-12: $l = 17 > l = 16$. $17 > 15$. $17 > 13$. $17 > 9$.
 $14 > 11$. $13 > 8$. $9 > 11$.

Comparisons from Hg₂I₂-4: $l = 13 > l = 7$. $4 > 3$. $0 > 11$.

Comparisons from Hg₂I₂-1: $l = 13 > l = 3$. $9 > 3$.

TABLE VI

RELATIVE VALUES OF THE STRUCTURE FACTOR FOR Hg_2I_2 CALCULATED FOR CERTAIN VALUES OF THE PARAMETERS AND OF $\overline{\text{Hg}}/\overline{\text{I}}$

	$\begin{matrix} u = 0.117 \\ v = .353 \end{matrix}$	$\begin{matrix} u = 0.116 \\ v = .347 \end{matrix}$	$\begin{matrix} u = 0.116 \\ v = .347 \end{matrix}$
	$\overline{\text{Hg}}/\overline{\text{I}} = 1.96$	$\overline{\text{I}} = 1.51$	$\overline{\text{Hg}}/\overline{\text{I}} = 1.96$
0	2.96	2.51	2.96
1	0.85	0.55	0.89
2	.08	.17	.12
3	.23	.10	.17
4	2.77	2.23	2.68
5	1.59	1.42	1.81
6	0.15	0.37	0.22
7	.16	.33	.16
8	2.25	1.52	1.93
9	2.30	2.17	2.60
11	0.29	0.27	0.09
13	2.79	2.50	2.96
14	0.33	0.45	0.77
15	.22	.18	.16
16	.76	.02	.27
17	2.96	2.29	2.74
	7 < 3	3,5,16 too low	7,11 too low
		7 < 6	17 < 13
		17 < 13	

TABLE VII

COMPARISON OF UNIT DISTANCES AND PARAMETERS OBTAINED BY DIFFERENT INVESTIGATORS

Hg_2Cl_2	a_0 , Å.	a_0 , Å.	u	v
Mauguin ⁹	4.45	10.90	0.125	0.375
Hylleras ¹⁰	4.45	10.88	.125	.375
Havighurst ¹¹	4.47	10.89	.110	.360
Havighurst ¹²			.116	.347
Hg_2Br_2				
Hylleras ¹⁰	4.67	11.16	.125	.375
Havighurst ¹¹	4.65	11.10	.108	.358
Havighurst ¹²			.116	.347
Hg_2I_2				
Hylleras ¹⁰	4.91	11.57	.125	.375
Havighurst ¹¹	4.92	11.61	.105	.355
Havighurst ¹²			.116	.347
Huggins and Magill	4.92	11.64	.117	.353

⁹ Mauguin, *Compt. rend.*, 178, 1913 (1924). From powder photographs.¹⁰ Hylleras, *Physik. Z.*, 26, 811 (1925). From powder photographs.¹¹ Havighurst, *Am. J. Sci.*, 10, 15 (1925). From powder photographs and ionization spectrometer measurements on Hg_2Cl_2 . The parameter values were calculated on the assumptions that $v - u = .250$ and that the Hg-Hg distance = 2.40 Å. in each case.¹² Havighurst, *THIS JOURNAL*, 48, 2113 (1926). The parameter values were obtained from calculations of the density of scattering power for x-rays at points on the tetragonal axis. These are undoubtedly more accurate than the earlier values.

of the atomic numbers (see Table VI). Although the true values of the parameters may differ slightly from these, greater differences than 0.01 would seem to be very improbable.¹³

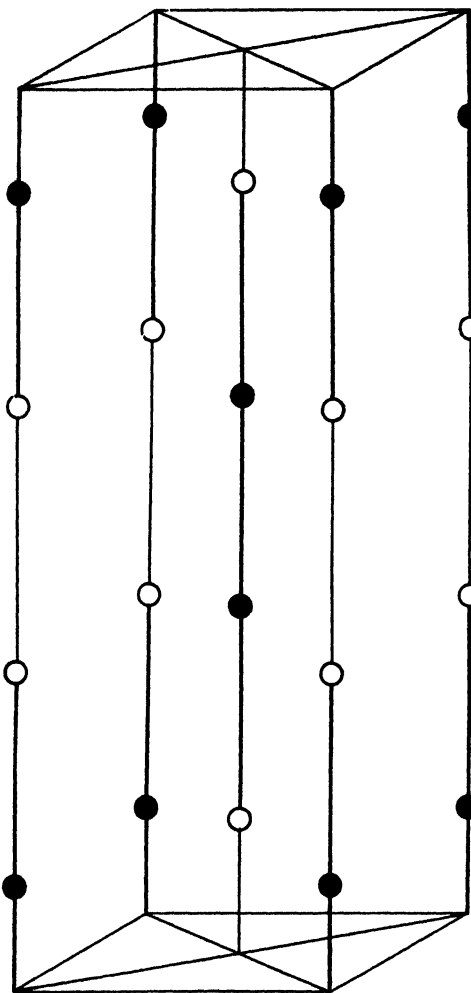


Fig. 3.—The unit cell of Hg_3I_2 .

Description and Discussion of the Structure

The arrangement of atomic centers within the unit cell is shown in Fig. 3. It is apparent that the structure can be considered as an aggregation of IHgHgI "molecules," so distributed as to surround each Hg atom by four I atoms in other molecules and *vice versa*. The shortest distances between atoms, calculated from our values of the unit distances and parameters, are as follows. Hg-Hg, 2.72 Å.; I-I, 3.42 Å.; Hg-I (on same tetragonal axis), 2.75 Å.; Hg-I (not on same tetragonal axis), 3.65 Å.

If there are two valence electrons per Hg atom and seven per I atom, there are just sufficient for a complete octet around each I kernel and a pair between each two adjacent Hg kernels. It would seem reasonable to assume that each I valence shell consists of four electron pairs tetrahedrally disposed, as in the case of HgI_2 , but the orientation of these tetrahedra cannot at present be determined.

¹³ For no combination of parameters and ratio of reflecting powers was complete agreement obtained. For this reason we thought it advisable to postpone publication until our comparisons could be checked by new data, and others obtained. Although up to the present time it has not seemed feasible to do this, further delay in publication would appear to be unnecessary, in view of the agreement between our results and those published by others. Havighurst's 1926 parameter values give no better agreement than ours, no matter what ratio of $\overline{\text{Hg}}/\overline{\text{I}}$ is assumed (see Table VI). The reason for the disagreement is probably that the assumption that the atoms can be treated as point-scatterers is probably not valid when considering reflections from very complicated planes.

Summary

The crystal structure of tetragonal HgI_2 has been determined, (a) using spectral photographic data alone, and (b) using data from Laue photographs, together with spectra from the (100), (110) and (001) planes. The unit (Fig. 1) has the dimensions $a_0 = 4.34 \text{ \AA.}$ and $c_0 = 12.34 \text{ \AA.}$ and contains Hg atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and I atoms at $(0, \frac{1}{2}, u)$, $(\frac{1}{2}, 0, \bar{u})$, $(\frac{1}{2}, 0, \frac{1}{2} - u)$ and $(0, \frac{1}{2}, u + \frac{1}{2})$, with $u = .140 \pm .003$. The valence electrons are probably in pairs at tetrahedron corners around both Hg and I atoms, each Hg being bonded to four I atoms and each I to two Hg atoms. The structure may be said to consist of "layer molecules." The interatomic distance (Hg-I) within each layer is 2.77 \AA. The shortest distance (I-I) between atoms in different layers is 4.10 \AA.

The unit of Hg_2I_2 is a tetragonal prism having the dimensions $a_0 = 4.92 \text{ \AA.}$ and $c_0 = 11.64 \text{ \AA.}$ Hg atoms are at $(0,0,u)$, $(0,0,\bar{u})$, $(\frac{1}{2}, \frac{1}{2}, u + \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - u)$; I atoms at $(0,0,v)$, $(0,0,\bar{v})$, $(\frac{1}{2}, \frac{1}{2}, v + \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - v)$; u and v being approximately .117 and .353, respectively. The structure (Fig. 3) is thus built up of IHgHgI molecules, within which the Hg-Hg and Hg-I distances are approximately 2.72 \AA. and 2.75 \AA. , respectively.

These results are in good agreement with those obtained by others.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

HYDROGEN GAS THERMOMETER COMPARED WITH THE OXYGEN AND HYDROGEN VAPOR-PRESSURE THERMOMETERS BY MEANS OF A COPPER-CONSTANTAN THERMOCOUPLE

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In connection with establishing a temperature scale for this Laboratory, a preceding paper² gives the results of comparison of copper-constantan thermocouples with the hydrogen gas thermometer from 15 to 283°K.

The present article presents results obtained by comparison of standard thermocouple W of Giaque, Buffington and Schulze (designated hereafter G., B. and S.) with the oxygen and hydrogen vapor-pressure thermometers.

The temperatures obtained from the oxygen vapor pressures as given by Cath³ are in very satisfactory agreement with those obtained from the thermocouple of G., B. and S. On the other hand, the results obtained by means of the hydrogen vapor-pressure measurements have fortunately

¹ National Research Fellow in Chemistry, University of California.

² Giaque, Buffington and Schulze, *THIS JOURNAL*, 49, 2343 (1927).

³ Cath, *Comm. Phys. Lab. Univ. Leiden*, 152d, 1918.

led to the prompt discovery of serious error in the hydrogen-gas thermometer results below 25°K. Our results indicate that considerable adsorption of the hydrogen gas must have taken place within the thermometer bulb, particularly at temperatures below the boiling point of hydrogen. This was not to be expected, since it had not been noted in the previous experience of others. The thermometer corrections for gas imperfection were taken from the work of Cath and Onnes⁴ in which duplicate bulbs containing hydrogen and helium, respectively, were kept in the same bath and differential pressures recorded. Corrections based on this method would include small adsorption effects. An important difference in the work of G., B. and S. was the use of a Pyrex glass thermometer bulb, whereas Cath and Onnes used one made from Jena glass.

The preparation of the Pyrex glass bulb used by G., B. and S. is perhaps worthy of comment. The bulb was blown and capillary tubing attached by means of a small opening which was left in the bottom until the bulb had been cleaned. Cleaning was accomplished by boiling in distilled water for some time, for one-half hour at least. The bulb was then dried by means of a stream of clean air and the bottom sealed off. We can remember no unusual surface condition resulting from the glass blowing but the apparatus has not been dismantled to confirm this.

There undoubtedly was a small amount of adsorbed water on the walls during the measurements, since the bulb was not heated during the pumping by the mercury diffusion pump. This adsorbed water could contribute no appreciable pressure, but is worth noting from the point of view of its possible effect on the character of the surface. At least until further work is carried out, the use of a Pyrex glass hydrogen thermometer below 25°K. must be regarded with suspicion. The most desirable change would be the use of helium gas.

Apparatus

The apparatus was that used by W. F. Giaque and R. Wiebe in an investigation to be published soon. Since the hydrogen thermometer described in the preceding paper was modeled after the above apparatus, the essential details and operation were practically identical, except that the thermometer bulb and the heavy cylinder which immediately surrounds it are replaced by a gold container connected with the exterior of the apparatus by means of a small glass tube with a platinum seal. The thermocouple was placed in the same manner as described in the preceding paper.

The pressure measurements were made in the same way, except that a manometer with tubes 1.6 cm. in diameter was used. All pressures are expressed in terms of international cms. of Hg. The gravitational

⁴ Cath and Onnes, *Comm. Phys. Lab. Univ. Leiden*, 156a, 1922.

acceleration used was 979.973 cm./sec.² as given by Sternwarte⁵ for this location.

Preparation of Oxygen

Electrolytic oxygen was prepared from a potassium hydroxide solution. It was freed from diffused hydrogen by passage over copper oxide maintained at 400°. The gas was then passed over amalgamated copper and solid potassium hydroxide. It was liquefied by means of liquid air and then fractionated, the middle third being used.

Oxygen Vapor-Pressure Results

The results of the oxygen vapor-pressure measurements are given in Table I, where they are compared with the temperatures given by the equation of Cath.³

$$\log_{10} P_{(\text{atmos.})} = \frac{-419.31}{T} + 5.2365 - 0.00648T \quad (1)$$

TABLE I
OXYGEN VAPOR-PRESSURE COMPARISON

P International cm. of Hg	T Equation (1)	T Thermocouple W
6.046	71.40	71.40
14.359	76.76	76.77
29.634	81.99	82.02
54.278	87.01	87.04
75.715	90.10	90.10

The agreement is better than we had expected and may indicate that the small deviations in the hydrogen gas thermometer comparison were due to the thermometer rather than to the thermocouple.

Preparation of Hydrogen

Electrolytic hydrogen was prepared in the manner described in the preceding paper, although in this case the purity is probably not important since impurities reasonably possible should not affect the vapor pressure appreciably.

Hydrogen Vapor-Pressure Results

The results of the measurements on hydrogen are given in Table II.

The readings of Thermocouple W are expressed in terms of Thermocouple Number 17 of G., B. and S. to facilitate comparison. The temperatures given in Col. 3 are calculated from the formula

$$\log_{10} P_{(\text{atmos.})} = -\frac{44.368}{T} + 1.6523 + 0.03240T - 0.0004189T^2 + 0.00000484T^3 \quad (2)$$

given by Martinez and Onnes.⁶

The thermocouple readings in the first two measurements given in Table II indicate too high a temperature, since a good vacuum had not

⁵ Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, 1923.

⁶ Martinez and Onnes, *Comm. Phys. Lab. Univ. Leiden*, 156b, 1922.

TABLE II
HYDROGEN VAPOR-PRESSURE COMPARISON

P International cm. of Hg	Thermocouple Microvolts	T Equation (2)	T Table III	T Calculated from data of G., B. and S.
2.687	6654.53	12.93 ^a	13.00	...
5.371	6650.52	13.92	13.96	(13.23)
31.090	6632.47	17.68	17.68	17.21
67.197	6619.60	19.95	19.96	19.66
74.822	6617.48	20.31	20.31	20.07
30.592	6632.80	17.64	17.62	17.14
30.984	6632.60	17.67	17.66	17.18
5.370	6650.71	13.92	13.91	(13.19)
5.368	6650.67	13.92	13.92	(13.20)

^a From equation (3).

been obtained when the readings were taken, and heat leak apparently influenced the thermocouple. The average value of the triple-point pressure, 5.370 cm., gives 13.92°K. as the temperature of the triple point. We have accepted this value in preference to the value of 13.95 given by Onnes and Gulik⁷ since there seems to have been some uncertainty as to the triple-point pressure (see Onnes and Keesom).⁸ However, our value for the triple-point pressure is in near agreement with that of Onnes and Braak,⁹ namely, 5.382 cm.

At 2.687 cm. pressure the hydrogen was solid and equation (2) could not be used. To find the temperature at this point the calorimetric data of Simon and Lange¹⁰ were used with the triple-point pressure and the temperature to obtain the equation

$$\log_{10} P_{(\text{cm.})} = \frac{-39.2}{T} + 2.70 \log T + 0.4584 \quad (3)$$

The procedure for obtaining equation (3) was to evaluate the two constants of Berthelot's equation of state by combining equation (2) with the thermodynamic equation $dP/dT = \Delta H/T\Delta V$ and the heat of vaporization data of Simon and Lange. With an equation of state thus established, combined with the calorimetric heat of sublimation and the assumption that infinitely dilute hydrogen gas would have the heat capacity of an ideal monatomic gas, equation (3) was readily obtained.

When the above thermocouple readings are compared with the data of G., B. and S. it is found that the temperatures given (Col. 5, Table II) are too low, which would be explained by adsorption in the gas thermometer. The character of the deviation makes the assumption of adsorption seem probable. Our values near the hydrogen boiling point

⁷ Onnes and Gulik, *Comm. Phys. Lab. Univ. Leiden*, 184, 1926.

⁸ Onnes and Keesom, *ibid.*, 137d, 1913.

⁹ Onnes and Braak, *ibid.*, 95e, 1906.

¹⁰ Simon and Lange, *Z. Physik*, 15, 312 (1923).

are rapidly approaching those of G., B. and S., indicating agreement a little above 25°K., while below the boiling point the effect rapidly increases, as would be expected. The agreement at 25°K. and in the range covered by the oxygen vapor pressures leads us to believe that the intermediate data of G., B. and S. are satisfactory.

The values given in Col. 4 are obtained by comparison with Table III,

TABLE III
TEMPERATURE CONVERSION TABLE

$T^{\circ}\text{K.}$		Diff.	$d\epsilon/dt$	Diff.
10	(6665.29)	(3.30)	(3.15)	(0.30)
11	(6661.99)	(3.59)	(3.45)	(.29)
12	(6658.40)	(3.89)	(3.74)	(.29)
13	6654.51	4.17	4.03	.29
14	6650.34	4.47	4.32	.29
15	6645.86	4.75	4.61	.28
16	6641.11	5.03	4.89	.28
17	6636.08	5.31	5.17	.27
18	6630.77	5.57	5.44	.27
19	6625.20	5.85	5.71	.27
20	6619.35	6.11	5.98	.26
21	6613.24	6.37	6.24	.26
22	6606.87	6.62	6.50	.25
23	6600.25	6.88	6.75	.25
24	6593.37	7.12	7.00	.25
25	6586.25	7.38	7.25	.25
26	6578.87	7.62	7.50	.25
27	6571.25	7.87	7.75	.24
28	6563.38	8.12	7.99	.25
29	6555.26	8.36	8.24	.24
30	6546.9		8.48	

which was constructed from the vapor-pressure data, and should be used to extend the table of G., B. and S. below 30°K.

It may be noted that no work based on the temperature scale of G., B. and S. has yet been published, so that the adsorption error encountered will result in no corrections to the literature.

Summary

One of the standard copper-constantan thermocouples described by Giaque, Buffington and Schulze in the preceding paper has been compared with the oxygen and hydrogen vapor-pressure thermometers.

Complete agreement, within the limits of accuracy, has been found with the Leiden scale at the temperatures of liquid oxygen.

The hydrogen vapor-pressure measurements have shown that the scale of G., B. and S. is in error below 25°K., apparently due to adsorption of hydrogen in the gas thermometer.

A table showing the behavior of a typical copper-constantan thermocouple below 30°K. has been given to extend that of G., B. and S.

The triple-point pressure of hydrogen was found to be 5.370 international cm. of Hg. This value, when combined with the vapor-pressure results of Martinez and Onnes, gives a triple-point temperature of 13.92°K.

An equation for the vapor pressure of solid hydrogen is included.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 141]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. I A BI-BVALENT SALT AND THE ION ATTRACTION THEORY

BY ULRIC B. BRAY¹

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Introduction

The ion attraction theory developed first by Milner,² and more recently by Debye and Hückel,^{3,4} has offered an apparently satisfactory explanation, at any rate at small concentrations, of the known behavior of strong electrolytes. The mathematical development of the theory shows why, and predicts how, the activity of an ion is related to the ionic strength. The equation for the activity coefficient γ of an ion with charge v as the ionic strength approaches zero is

$$\log \gamma = -Av^2 \sqrt{\frac{1}{2} \Sigma mv^2} \quad (1)$$

¹ National Research Council Fellow in Chemistry.

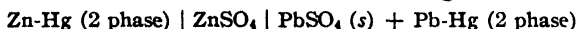
² Milner, *Phil. Mag.*, **23**, 551 (1912); *ibid.*, **25**, 742 (1913).

³ (a) Debye and Hückel, *Phys. Z.*, **24**, 185 (1923); (b) Debye, *ibid.*, **24**, 334 (1923).

⁴ For a clear and critical presentation of this theory see A. A. Noyes, *THIS JOURNAL*, **46**, 1080 (1924).

In this expression A is composed of certain universal constants, the dielectric constant, D_0 , of the solvent, and the absolute temperature. Using Drude's value, 78.77, for D_0 for water at 25° , the coefficient A becomes 0.505; using the recent value, 77.81, given by Kockel,⁵ A becomes 0.514. La Mer, King and Mason⁶ have obtained experimentally the value 0.528 for A from solubility measurements on the sparingly soluble tri-trivalent salt luteo-cobalt ferrocyanide and have calculated activity ratios for this salt which agree excellently with the theory.

In order to test the theory further with electrolytes of high-valence type, the activity coefficients of the bi-bivalent salt zinc sulfate were determined through electromotive-force measurements. Using the cell



measurements were made over the concentration range from 0.0006 to 3.4 molal. The electromotive force E of the cell in terms of its electromotive force E_0 when the activities of the zinc and sulfate ions are 1 molal is related to the mean activity coefficient of the ions of the salt $\sqrt{\gamma_{\text{Zn}} \gamma_{\text{SO}_4}}$ and to its molality, m , as follows

$$E = E_0 - 0.059150 \log m \sqrt{\gamma_{\text{Zn}} \gamma_{\text{SO}_4}} \quad (2)$$

For the convenience in plotting and calculating the mean activity coefficient we shall calculate the value of the quantity E'_0 defined by the equation

$$E'_0 = E + 0.059150 \log m \quad (3)$$

Combined with (2) this gives

$$E'_0 = E_0 - 0.059150 \log \sqrt{\gamma_{\text{Zn}} \gamma_{\text{SO}_4}} \quad (4)$$

From Equation 1, using Kockel's value for D_0 , we get for the bivalent salt

$$\log \sqrt{\gamma_{\text{Zn}} \gamma_{\text{SO}_4}} = -4.11 \sqrt{m} \quad (5)$$

Combining this with (4), we obtain

$$E'_0 = E_0 - 0.243 \sqrt{m} \quad (6)$$

It is evident that a plot of E'_0 against m should, as zero concentration is approached, give a straight line with slope -0.243 , and that the correct extrapolation of the curve to zero will give E_0 . Since the approach to linearity and the final slope constitute the test of the limiting equation, it was the author's purpose to determine this slope more accurately and with less uncertainty than has previously been possible from electromotive-force or freezing-point data.

Apparatus and Method

The Cell and Electrodes.—Although the attempts of some previous investigators^{7,8} to use a lead-lead sulfate electrode were unsuccessful,

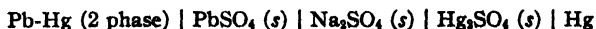
⁵ Kockel, *Ann. Physik*, [4] 77, 417 (1925).

⁶ La Mer, King and Mason, *THIS JOURNAL*, 49, 363 (1927).

⁷ Lewis and Brighton, *ibid.*, 39, 1906 (1917).

⁸ Horsch, *ibid.*, 41, 1788 (1919).

Henderson and Stegeman⁹ obtained very constant and reproducible results with the cell



A careful study of lead-lead sulfate electrodes was made by the present author, which led to the following conclusions: (1) oxygen must be excluded from the cell; (2) a definite, crystalline form of lead sulfate is essential; (3) equilibrium between the solid lead sulfate and the solution

is best established before the electrode is made up; (4) the use of a two-phase amalgam is desirable.

Fig. 1 shows diagrammatically the cell vessel used. The tubes marked N permitted nitrogen to be passed through the solution and were connected to glass manifolds by bits of rubber tubing carrying screw pinch-cocks for equalizing the flow of gas in the different electrodes. A mercury trap on the outlet manifold prevented the diffusion of air into the cell when the flow of nitrogen was stopped. The passage of nitrogen through the cell served the double purpose of removing oxygen and of stirring the contents of the cell above the amalgams. The platinum wires sealed into the bottoms of the electrodes were fused to copper wires, eliminating the inconvenient use of mercury for electrical contacts to the measuring system. By using fairly small platinum wire, 0.4 mm. diameter, platinum-Pyrex seals may be made to hold satisfactorily. During the course of the experiments there has been no difficulty encountered from leakage through these seals.

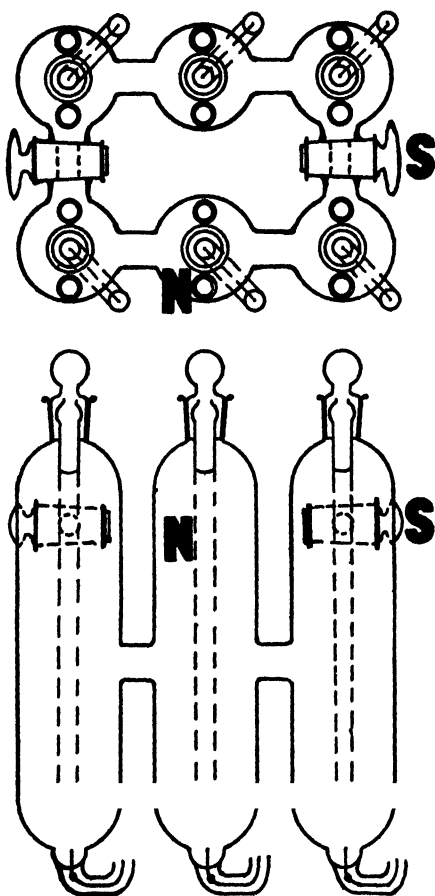


Fig. 1.

Since the preparation of a satisfactory sulfate electrode for use in dilute solution requires attention to certain details, it seems desirable to describe the technique employed. The zinc sulfate solution to be used was first divided into two parts. To one part was added several grams of lead sulfate previously washed with the same solution, and the mixture

⁹ Henderson and Stegeman, *THIS JOURNAL*, 40, 84 (1918).

in a 1-liter, glass-stoppered, Jena glass bottle was rotated for 12–15 hours. At the end of this time, the electrode vessel, which had been dried at 115° , was filled with nitrogen by running a rapid stream of the gas through it for 5–10 minutes. The two-phase amalgams were heated until they became one-phase and were pipetted into the electrode vessel. Pyrex pipets of about 15 cc. capacity with an ungreased stopcock on the lower tube were used. A stream of nitrogen was passed through the cell while the amalgams cooled to room temperature. The half of the vessel containing the lead amalgam was filled with the solution saturated with lead sulfate after a layer of lead sulfate from the bottom of the flask had been pipetted onto the lead amalgam. The half containing the zinc amalgam was filled with the remainder of the solution which had not been saturated with lead sulfate. Large stopcocks and short tubes at S made it possible to make readings with the stopcocks closed in all but the two lowest concentrations. At these concentrations the initial level of liquid in the zinc side was made higher than in the lead side in order that when the stopcocks were opened for a reading the slight flow of solution would be from zinc to lead and never the reverse. After the cell had been placed in the thermostat, nitrogen was passed through for two hours. At the end of this time the cell had reached the temperature of the thermostat and its electromotive force was generally within less than a millivolt of the final constant reading.

The cell vessel (Fig. 1) is composed of six electrodes divided into two groups of three by the two stopcocks, S. On the one side, three similar lead sulfate electrodes were made and, on the other side, three zinc electrodes. The six external wires were connected to the potentiometer through a switchboard which permitted any pair of electrodes to be compared. The triplicate lead and triplicate zinc electrodes furnished a convenient and satisfactory check on the constancy and the reproducibility of the cell. In all of the experiments the zinc electrodes were found to check each other within 0.03 millivolt, and the sulfate electrodes to within 0.04 millivolt. Readings were taken on each cell over at least 36 hours after the cell had reached its final value (which was generally within six hours after the cell was made); and the degree of constancy obtained was such that the average reading of the combinations remained constant to within 0.04 millivolt over this period of time. In some of the experiments the cells were allowed to remain in the thermostat for a week before the divergence from the mean became as great as 0.2 millivolt.

In all solutions below 0.02 molal, another check on the cells was made by pipetting off the solution above the amalgams after the cell had been read for two days and introducing fresh solution. In four or five hours the cell would always come back to its previous reading.

Analysis of Zinc Solutions.—For experiments below 1 molal concen-

tration two stock solutions of zinc sulfate were used. Into a weighed quantity of solution, a sufficient quantity of redistilled water was weighed. The stock solutions were analyzed by titrating potentiometrically with potassium ferrocyanide solution (twentieth molal, to each liter of which had been added 1 g. of potassium ferricyanide). A bright platinum wire and calomel electrode comprised the electrodes. A weighed sample of the solution was made acid with 5 cc. of 4 *N* sulfuric acid, diluted to 250 cc., heated to 70° and stirred while the titration was being made. With reasonable care this method of zinc analysis is good to 0.1%; often three or four check analyses will have a deviation of less than 0.05%. The potassium ferrocyanide solution was standardized, first, against Kahlbaum's "zur Analyse" zinc sticks scraped clean; second, by titrating the zinc sulfate

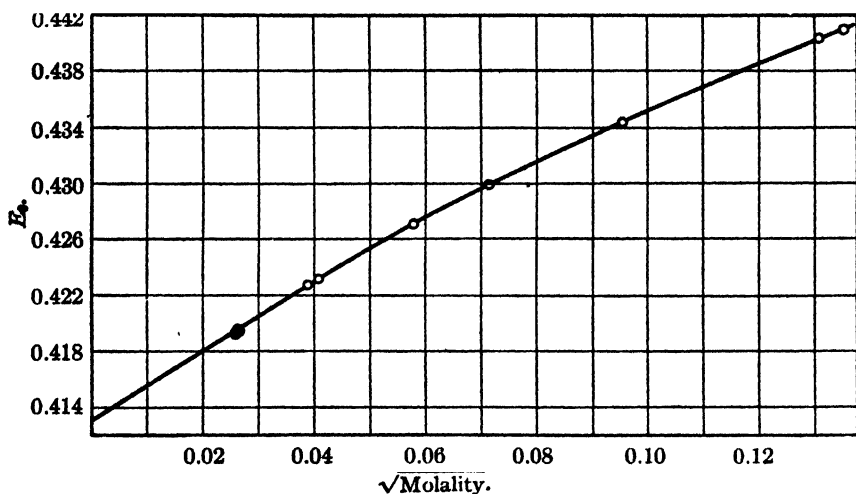


Fig. 2.—The zinc-lead cell at small concentrations.

residue left in a weighed platinum dish upon evaporation of a concentrated solution of zinc sulfate and heating the dish to 500°. The first method is the more exact but the second method was found to check to within 0.2%.

The Measurements.—All measurements were made at $25.00 \pm 0.01^\circ$ in an oil-bath heated with a nichrome coil. The potentiometer was a Leeds and Northrup type K with Leeds and Northrup galvanometer No. 2500 B of resistance 460 ohms. The Weston standard cell used was checked at regular intervals against the laboratory standard cell.

Preparation of Materials

Lead Nitrate.—Merck's best grade of c. p. salt was recrystallized three times from hot water and the crystals were dried in air.

Lead Sulfate.—Since the lead sulfate was to be used in zinc sulfate solution, it was considered advisable to precipitate the lead sulfate with zinc sulfate. To a 5% solution of lead nitrate, made from the purified lead nitrate, was added an excess of a 10% solution of purified zinc sulfate. The liquid with its precipitate was heated to boiling

and boiled for fifteen minutes, after which time the lead sulfate had assumed a definite, crystalline form. The lead sulfate was washed ten times by decantation and drained on a Buchner funnel. The material was then transferred to a wide-mouthed bottle and kept under distilled water until used. The author has found that in any case where a solid material is to be used for electrodes it is advisable to keep the material under water until it is used.

Zinc Sulfate.—The best grade of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was recrystallized three times from hot water. According to Mellor¹⁰ the maximum solubility of zinc sulfate is at 70°. The heptahydrate obtained on slowly cooling the solution was partially dried in air.

Lead Amalgam.—Into mercury which had been carefully purified¹¹ lead was electrolyzed from a solution of lead nitrate. The anode consisted of platinum foil placed in another beaker filled with 1 *N* HNO_3 , and connected to the first beaker by means of a Y-tube. A paddle stirrer was placed in the mercury in the cathode beaker so as to slowly stir the mercury during the electrolysis. The current was 0.1 ampere and was run until the concentration of lead in the amalgam was about 3%. The amalgam was washed, dried and heated until it became one-phase and filtered through a capillary tube into an evacuated flask which was then filled with nitrogen.

Zinc Amalgam.—Sticks of Kahlbaum's "zur Analyse" grade of zinc were purified by rapid electrolysis with 3–4 amperes. The zinc crystals were washed, drained and weighed moist. A weighed quantity of mercury corresponding to 3% zinc was added to the moist crystals; the mass was then covered with a dilute solution of nitric acid and stirred until all the zinc crystals had gone into the amalgam. After washing, drying, heating and filtering through a capillary tube into a vacuum the amalgam was stored under nitrogen in the same way as the lead.

Nitrogen.—Tank nitrogen was purified by the van Brunt method.¹² The gas after leaving the dilute sulfuric acid wash bottle was dried by passing through a tower filled with soda lime. Passing through a three-way stopcock, the gas was used dry or led into a bubbler filled with a zinc sulfate solution of the concentration used in the cell and thence into the cell vessel.

The Experimental Data

In Table I are given the experimental data and the calculated function E'_0 . The observed electromotive forces given in Col. 2 are in every case the average of the combination of the six electrodes described above.¹³

¹⁰ Mellor, "Inorganic and Theoretical Chemistry," Longmans and Co., London, 1923, Vol. IV, p. 614.

¹¹ Fay and North, *Am. Chem. J.*, **25**, 216 (1901).

¹² Van Brunt, *THIS JOURNAL*, **36**, 1448 (1914).

¹³ A correction for the solubility of lead sulfate was made at the concentrations of 0.003 *M* and less. This was done by calculating the increase in sulfate-ion concentration in the solution coming from the solubility of lead sulfate, and by obtaining the corresponding potential resulting therefrom by means of the usual equation $E = 0.0296 \log c_1/c_2$. Böttger (*Z. phys. Chem.*, **46**, 804 (1903)) found the solubility of lead sulfate at 25° to be 1.34×10^{-4} *M*. From the limiting ion attraction equation, γ is found to be 0.88 at this concentration, so that the solubility product of lead sulfate is 1.39×10^{-8} . From the quadratic equation $(\gamma m + x)x = 1.39 \times 10^{-8}$, by substituting the values of γ calculated from the limiting equation, the value of the increase x in the sulfate-ion concentration due to the lead sulfate was obtained and, by completing the calculations indicated above, we get the following corrections which have been added to the observed voltages: 0.0033 *M*, 0.00004 v.; 0.0016 *M*, 0.00012 v.; 0.0015 *M*, 0.00013 v.; 0.00069 *M*, 0.00055 v.; 0.00067 *M*, 0.00058 v.; 0.00066 *M*, 0.00059 v.

TABLE I
THE OBSERVED ELECTROMOTIVE FORCES OF THE ZINC-LEAD CELL AT 25°C.

Molality, <i>M</i> per 1000 g. of H ₂ O	Electromotive force <i>E</i>	<i>E'</i> ₀
0.0006580	0.60744	0.41924
.0006699	.60723	.41949
.0006866	.60671	.41960
.0007016	.60603	.41949
.001505	.58978	.42283
.001648	.58783	.42321
.003322	.57374	.42713
.005064	.56576	.42996
.009096	.55520	.43447
.01712	.54490	.44041
.01824	.54391	.44105
.04120	.53175	.44982
.08532	.52114	.45801
.1732	.51219	.46715
.2532	.50766	.47237
.3518	.50366	.47682
.8564	.49320	.48922
1.426	.48585	.49497
2.052	.47827	.49674
2.749	.46855	.49453
3.419	.45811	.48969

TABLE II
THE MEAN ACTIVITY COEFFICIENTS OF ZINC SULFATE AT 25°

Molality, <i>M</i>	E.m.f., <i>E'</i> ₀	Mean activity coefficients of Zn ⁺⁺ and SO ₄ ⁻⁻		
		From e.m.f.	From ion attraction theory	Percentage difference
0.0001	0.41553	0.907	0.910	+0.3
.0005	.41866	.803	.809	+ .7
.001	.42097	.734	.741	+1.0
.002	.42410	.650	.654	+0.6
.005	.42985	.519	.512	-1.3
.01	.43528	.421	.388	-7.8
.02	.44196	.324	.262	-19.1
.05	.45190	.220	.120	-45.4
.08	.45762	.176		
.1	.45991	.161		
.2	.46905	.113		
.3	.47460	.0910		
.5	.48172	.0690		
.8	.48830	.0534		
1.0	.49120	.0477		
1.5	.49538	.0405		
2.0	.49670	.0385		
2.5	.49569	.0400		
3.0	.49295	.0445		
3.5	.48907	.0518		

As a final check on the measurements in the very dilute solutions, a flowing electrode using a dilute (0.03%) zinc amalgam was employed in the zinc half-cell for the concentrations 0.001505 *M* and 0.0007016 *M*. The potential of this dilute amalgam electrode against the two-phase zinc amalgam electrode was found to be 0.04750 volt. The voltages given in the table for the two cells referred to are corrected for this difference.

From a large-scale plot of E'_0 against \sqrt{m} , values of E'_0 at round concentrations were read, and the corresponding mean activity coefficients⁹ were calculated by Equation 4, using the value of E_0 determined by the extrapolation described below. These values are given in Table II along with the coefficients calculated from the ion-attraction theory, using Kockel's value for $A = 0.514$ up to where the percentage deviation from the limiting equation becomes enormous.

Discussion of the Results

The experimental values of E'_0 fall so well upon a smooth curve which rapidly approaches linearity below 0.01 *M* that the final slope can be determined with almost no ambiguity by plotting the slope of the curve at even intervals against the corresponding value of \sqrt{m} and obtaining the constant value approached in the most dilute solutions. This final slope is found to be -0.248 , which corresponds to 0.523 for the value of A in Equation 1.

Extrapolating the E'_0/\sqrt{m} curve to zero concentration asymptotic to a straight line with this slope of -0.248 , the electromotive force of the cell when the zinc ions and sulfate ions have activities of 1 molal is found to be 0.41302 volt.

The validity of the ion attraction theory at small concentrations is also made evident by the agreement of the experimental and theoretical activity coefficients given in Table II. Up to 0.005 molal (an ionic strength of 0.02) the agreement is within 2%, and perhaps within the experimental error. This is a very striking fact when it is considered that at 0.005 molal the activity coefficient has already fallen to nearly 0.5.

A scarcely less striking fact is the rapidity with which, as the molality further increases, the actual activity coefficients deviate from those calculated by the limiting equation of the ion attraction theory. Thus, at 0.02 molal the deviation is already 19.1% and at 0.05 molal it is 45.4%. These results illustrate the great error that is made in applying mass-action equations that assume complete ionization and ion activities calculated even by the Debye-Hückel equation to equilibria involving bivalent ions at normalities greater than 0.01 normal. They also show that the theoretical corrections that must be introduced into the limiting equation of the ion attraction theory to make it apply at even moderate

concentrations must be such as will account for the very large deviations in the case of ions of higher valence.

That these corrections cannot consist merely in taking into account the size a of the ion by introducing a factor $(1 + Ba \sqrt{\Sigma mv^2})$ is indicated by the slow increase of this function with the ionic strength. It has indeed been shown by La Mer⁸ and his co-workers and by Schärer¹⁴ that the observed solubility effects cannot be accounted for in this way.

The author wishes to express his appreciation to Professor A. A. Noyes for his interest and helpful suggestions in carrying out this research.

Summary

The preparation of a reproducible lead-lead sulfate electrode has been described. Electromotive-force measurements at 25° on the cell Zn-Hg (2-phase) | ZnSO₄ | PbSO₄ (s) | Pb-Hg (2-phase) have been given over the concentration range 0.0006 to 3.4 molal. The potential of the cell when the ion activities are 1 molal has been found to be 0.41302 volt.

The mean ion activity coefficients for zinc sulfate through this concentration range have been calculated. The rapid decrease of these activity coefficients with increasing concentration is striking. Thus, the value has become 0.42 at 0.01 molal and 0.16 at 0.1 molal.

The experimental results at small concentrations are found to be in good agreement with the limiting equation of the ion-attraction theory. Thus the experimentally found value for the constant in the equation is 0.523, while the calculated value is 0.504 or 0.514, depending on whether Drude's or Kockel's value for the dielectric constant of water is used.

At molalities above 0.005 the deviations between the theoretical and observed values increase with extraordinary rapidity, showing that in the case of ions of higher valence the theoretical equation must have very substantial corrections applied to it, besides that of taking into account the size of the ions.

PASADENA, CALIFORNIA

¹⁴ Schärer, *Physik. Z.*, 25, 145 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM. X. THE
"ISOMERIC" CHLORIDES

BY JAS. LEWIS HOWE

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When in 1844 Claus¹ discovered ruthenium, he prepared two double chlorides with potassium, to which he assigned the formulas K_2RuCl_5 and K_2RuCl_6 . The first was formed when the precipitated oxide of ruthenium, or the volatile tetroxide, was dissolved in hydrochloric acid and treated with potassium chloride; the second when aqua regia was used. This was quite in harmony with salts of the other platinum metals. Claus also assigned the probable formula of $RuCl_2$ to the compound giving a conspicuous blue color when ruthenium solutions are treated with zinc, hydrogen sulfide or other strong reducing agents.

Later² it was shown that the supposed K_2RuCl_6 was a nitroso salt, K_2RuCl_5NO , which contains nearly the same percentage of ruthenium. The error of Claus was occasioned by his having determined the chlorine only by loss, and by having considered the atomic weight of ruthenium as 104.57.

The first salt has since the days of Claus passed for K_2RuCl_6 , a pentachloro-ruthenite, though the corresponding cesium and rubidium salts have appeared to be monohydrates, and a monohydrate of the potassium salt has also been described.³ No efforts to oxidize this salt to K_2RuCl_6 have been effective.

Later, Howe⁴ described a new monohydrate of K_2RuCl_5 , which differed very markedly from the former salt in properties, especially in stability toward hydrolysis and in being converted into K_2RuCl_6 by the action of chlorine. This was formed from the earlier K_2RuCl_5 by boiling with dilute alcohol in acid solution, and was called an "aquo" salt. The corresponding rubidium and cesium salts were also prepared, as well as similar salts with bromine⁵ in the place of chlorine. Attention was called to the apparent isomerism between these two series of pentachloro-ruthenites.

The composition of the blue compound, supposed by Claus to be $RuCl_2$, was considered by Joly⁶ to be $RuCl_2OH$, but in our work in this Laboratory⁷

¹ Claus, *Bull. acad. sci., St. Petersburg*, 3, 38, 311, 354 (1845).

² (a) Joly, *Compt. rend.*, 107, 998 (1888); (b) 108, 854 (1889). (c) Howe, *THIS JOURNAL*, 16, 388 (1894).

³ Miolati and Tagiuri, *Gazz. chim. ital.*, 30 (II), 511 (1900).

⁴ Howe, *THIS JOURNAL*, 26, 543 (1904).

⁵ Howe, *ibid.*, 26, 942 (1904).

⁶ Joly, *Compt. rend.*, 114, 291 (1892).

⁷ Howe, Howe, Jr., and Ogburn, *THIS JOURNAL*, 46, 335 (1924).

we satisfied ourselves that the compound contains bivalent ruthenium, and is RuCl_2 as Claus inferred, or at least $(\text{RuCl}_2)_x$. Remy⁸ has more recently considered it to contain univalent ruthenium, basing his opinion on its being formed by the reduction of K_2RuCl_6 , two units, as measured by the action of sodium amalgam. Zintl and Zaimis⁹ also assume univalent ruthenium in the blue solution, basing their view on the potentiometric titration of " RuCl_3 " with CrSO_4 or $\text{Ti}_2(\text{SO}_4)_3$, where with one equivalent they obtain a pale yellow solution, while with the next drop the blue begins to appear.

There are thus two problems insufficiently cleared up in connection with the chlorides of ruthenium, (1) the apparent isomerism in the K_2RuCl_6 series and (2) the valence of ruthenium in the blue compound.

Aoyama¹⁰ proposed calling the original K_2RuCl_6 the *alpha* salt, the dehydrated "aquo" salt *beta*, and added a third isomer, formed by the dechlorination of the hexachloro salt, K_2RuCl_6 , in hydrogen chloride gas, which he called a *gamma* salt. Gutbier,¹¹ however, showed that the *beta* and *gamma* salts are identical, and that both, when dissolved in dilute HCl , crystallize out as the "aquo" salt. The *alpha* and *beta* salts he considered to be isomers.

Briggs¹² accounts for the seeming isomerism by assigning the formula $2\text{K}_2\text{RuCl}_6 \cdot 3\text{H}_2\text{O}$ to the "aquo" salt. He states that the water should be weighed directly and not determined by loss, and that the salt must be heated in oxygen, since heating in air gives low results for the water. It is quite true that heating in air gives lower results than heating in oxygen, but the results in air check, especially in the case of the cesium salt, for the formula originally proposed for the "aquo" salt, $\text{Cs}_2\text{RuCl}_6 \cdot \text{H}_2\text{O}$. When heated in oxygen, ruthenium is slightly oxidized to the volatile tetroxide, which may account for the higher results of Briggs.

The reaction between hydrochloric acid and ruthenium tetroxide has been studied by a number of workers in the effort to throw light upon the chlorides. When the volatile tetroxide is collected in hydrochloric acid and potassium chloride added, the ordinary pentachloro salt is obtained, with the ratio K_2RuCl_6 , and this has generally been accepted as containing trivalent ruthenium, though there has been but a single attempt¹³ to verify this. Howe¹⁴ found that by the action of a solution of cesium chloride in concentrated hydrochloric acid a salt was obtained with the formula $\text{Cs}_2\text{RuO}_2\text{Cl}_4$, which is quite unstable; a similar osmium salt was obtained

⁸ Remy and Wagner, *Ber.*, 60, 493 (1927).

⁹ Zintl and Zaimis, *Ber.*, 60, 842 (1927).

¹⁰ Aoyama, *Z. anorg. Chem.*, 138, 249 (1924).

¹¹ Gutbier and Niemann, *ibid.*, 141, 312 (1925).

¹² Briggs, *J. Chem. Soc.*, 127, 1042 (1925).

¹³ Charonnat, *Compt. rend.*, 180, 1271 (1925).

¹⁴ Howe, *THIS JOURNAL*, 23, 779 (1901).

by Wintrebert.¹⁵ The free acid of the ruthenium salt, $\text{H}_2\text{RuO}_2\text{Cl}_4 \cdot 3\text{H}_2\text{O}$, was prepared by Aoyama¹⁰ by the action of hydrogen chloride gas on the tetroxide. Krauss¹⁶ let RuO_4 act on hydrochloric acid and potassium iodide and estimated the liberated iodine, finding that the ruthenium was reduced five units, that is, apparently, to K_2RuCl_5 . On the other hand, he^{16a} and others¹⁷ have obtained hexachloro-ruthenates, M_2RuCl_6 , either directly from RuO_4 or from the K_2RuO_4 in the peroxide melt; but the conditions of formation of the hexachloro-ruthenates have not been reproducible, and treatment of the "aquo" salts with chlorine has been relied on to prepare these salts. The hexabromo salts have been prepared in an analogous way.

Some two years ago, Charonnat¹³ suggested that the true formula for the ordinary pentachloro salt is $\text{K}_2\text{RuCl}_5\text{OH}$, basing his view upon the action of this salt on potassium iodide, and on the formation of the "aquo" salt by the action of hydrochloric acid on the oxalato-ruthenite, $\text{K}_3\text{Ru}(\text{C}_2\text{O}_4)_3$, in which the ruthenium is undoubtedly trivalent. Owing to lack of any details or analyses, and to the fact that most other ruthenium salts give pentachloro salts on treatment with hydrochloric acid, his view, though correct, has not obtained recognition; to Charonnat belongs the credit for the final solution of this perplexing problem. The fact that the pentachloro salt liberates iodine from potassium iodide has long been known, and Gall and Lehmann¹⁸ have studied this reaction with a view to its analytical possibilities. They have concluded that there is an equilibrium, $\text{RuCl}_3 + \text{HI} \rightleftharpoons \text{RuCl}_2 + \text{HCl} + \text{I}$, which seems to be the case.

This reaction between the pentachloro salt and potassium iodide has recently been worked on in this Laboratory in the effort to complete the third step¹⁹ in the determination of ruthenium, namely, to determine the ruthenium in the RuO_4 distillate. Failing to obtain satisfactory results with potassium iodide, evidently because of the above equilibrium, stannous chloride was tried, and in this work the surprising result was obtained that both K_2RuCl_5 and K_2RuCl_6 were each reduced one unit, and each gave the "aquo" salt on its reduction. In other words, *the valence of ruthenium is four, not only in K_2RuCl_6 , but also in what has always passed for K_2RuCl_5* . The formula of the latter salt proves to be $\text{K}_2\text{RuCl}_5\text{OH}$, as suggested by Charonnat, and it is a one-fourth hydrolyzed hexachloro-ruthenate. This was established both by analysis and also by recrystallization. $\text{K}_2\text{RuCl}_5\text{OH}$ was recrystallized from very concentrated hydrochloric acid and K_2RuCl_6 obtained, while when K_2RuCl_6 was re-

¹⁵ Wintrebert, *Thesis*, Bordeaux, 1902.

¹⁶ (a) Krauss, *Z. anorg. Chem.*, **117**, 111 (1921); (b) **136**, 62 (1924).

¹⁷ Howe, *THIS JOURNAL*, **23**, 784 (1901), Analysis 11.

¹⁸ Gall and Lehmann, *Ber.*, **59**, 2856 (1926).

¹⁹ Howe and Mercer, *THIS JOURNAL*, **47**, 2931 (1925).

crystallized from a less concentrated hydrochloric acid (under 6–8 *N*), the product was K_2RuCl_5OH . Since this is the ordinarily obtained compound of ruthenium, it would seem probable that the hydrated oxide of ruthenium, usually considered to be $Ru_2O_3 \cdot xH_2O$, is really $RuO_3 \cdot xH_2O$, since its solution always leads to H_2RuCl_5OH .

This also clears up the formation of the "aquo" salt, which is now to be recognized as the ordinary salt of trivalent ruthenium. Of the many different substances used in its formation,²⁰ such as alcohol, glucose, stannous chloride, etc., all are reducing agents, and the reaction is merely the reduction of quadrivalent to trivalent ruthenium. In some cases, as with alcohol, the reduction is slow, and has often failed to go to completion, resulting in impure salts and aberrant analyses. This also explains the ready oxidizability of the "aquo" salt to the hexachloro salt by chlorine, and why the hexachloro salt could not be formed from the pentachloro salt by oxidation.

It further follows from this work that the ruthenium in the blue solution is bivalent, since it is formed by reducing $Ru^{IV}Cl_5OH$ (H_2RuCl_5OH) two units. The yellow solution obtained by Zintl and Zaimis⁹ by its reduction one unit was the solution of the trivalent "aquo" salt.

The following chloro salts of ruthenium would thus seem to be well established; in most of the cases the corresponding bromo salts have also been prepared and are wholly analogous.

A. $M_2Ru^{VI}O_2Cl_4$ ($M = H, Rb, Cs$); the hydrogen salt formed by the action of gaseous hydrogen chloride on RuO_4 ; the rubidium and cesium salts by the action of rubidium or cesium chloride solution in very concentrated hydrochloric acid on RuO_4 .

B. $M_2Ru^{IV}Cl_6$ ($M = NH_4, K, Rb, Cs$); formed by the action of chlorine on $M_2Ru^{III}Cl_5 \cdot H_2O$; by action of very dilute cold hydrochloric acid on the K_2RuO_4 melt;²¹ by recrystallization of $M_2Ru^{IV}Cl_5OH$ from concentrated hydrochloric acid.

B(a). $Cs_2Ru^{IV}Cl_6 \cdot H_2O$; formed by the action of a solution of cesium chloride on a solution of RuO_4 in hydrochloric acid;²² efforts to obtain the rubidium and potassium hydrated salts in pure form were not successful.

C. $M_2Ru^{IV}Cl_5OH$ ($M = NH_4, K, Rb, Cs$); formed whenever a solution of RuO_4 in hydrochloric acid (except in very concentrated acid) is treated with an alkali chloride; when a solution of a ruthenate, M_2RuO_4 , is treated with hydrochloric acid; when the solution of any oxide of ruthenium, except one precipitated from the "aquo" salt, in hydrochloric acid is treated with an alkali chloride; when a hexachloro-ruthenate,

²⁰ Howe and Haynes, *THIS JOURNAL*, 47, 2924 (1925).

²¹ Antony and Lucchesi, *Gazz. chim. ital.*, 29 (II), 82 (1899); see also private communication from Antony, *THIS JOURNAL*, 26, 546 (1904).

²² Ref. 16 (a), p. 117.

$M_2Ru^{IV}Cl_6$ is recrystallized from hydrochloric acid, unless the latter is very concentrated.

D. $M_2Ru^{III}Cl_6 \cdot H_2O$ ($M = NH_4, K, Rb, Cs$); formed by the reduction of any of the salts of quadrivalent ruthenium in hydrochloric acid solution by alcohol, oxalic acid or other organic substance, stannous chloride or potassium iodide; also by the spontaneous oxidation in the air of the blue solution of bivalent ruthenium.¹⁷ These are the only crystalline salts of trivalent ruthenium, and are properly called pentachloro-ruthenites (rutheniat of Gutbier). It might be wise, however, to continue the use of the term "aquo"-ruthenites to distinguish them from the old pentachloro-ruthenites, which now become pentachloro-(hydroxy-)ruthenates.

E. $M_2Ru^{III}Cl_6$; formed only by the dehydration of the "aquo" salt, or dechlorination of the hexachloro-ruthenates (Aoyama's *gamma* and *beta* salts). These have not been obtained in a crystallized form and cannot, of course, be regarded as definite salts with a coordination number of five, but are of the same nature as the K_2SO_4 and $Al_2(SO_4)_3$ in dehydrated alum.

In all of these salts ruthenium has a coordination number of six and thus one of the few remaining compounds with an apparent coordination number of five is deleted from the list.

Experimental Work

The starting point of all the work described in this paper was ruthenium tetroxide, distilled by a current of chlorine from an alkaline sodium hypochlorite solution of various ruthenium compounds and residues. As the material was free from osmium, the purity of the ruthenium obtained was assured. The hypochlorite solutions were placed in a tubulated retort, chlorine (from a chlorine cylinder) led in until the deep red color of the ruthenate changed into the golden yellow of the tetroxide, when the chlorine stream was cut off and the retort rapidly heated to boiling. The RuO_4 passed over with the steam and was collected in a small amount of concentrated hydrochloric acid in an Erlenmeyer flask immersed in ice-water. With care no loss of the tetroxide occurred. On standing, the RuO_4 was completely converted into either H_2RuCl_6 or H_2RuCl_5OH , according to the concentration of the hydrochloric acid. If the amount of the RuO_4 is small, it dissolves in the hydrochloric acid and the conversion into the chloride is rapid; if the amount is larger, it collects in drops of liquid RuO_4 , which dissolve only slowly. The solutions of the chloride were concentrated to any desired degree and the salts formed by the addition of alkali chloride. If the solutions were quite concentrated, the salts precipitated on addition of the chloride; if more dilute the crystalline salts were obtained on evaporation. A similar procedure was used for recrystallization of the salts, these being dissolved in hot

water sufficiently acidified with hydrochloric acid to prevent further hydrolysis. For the preparation of the "aquo" salts, solutions of quadrivalent ruthenium, either of the acid or of the salts, were boiled in rather dilute condition with about one-fourth their volume of alcohol until the lightening of the color indicated reduction to trivalent ruthenium. Often the reduction was not complete, as was later revealed both by color and by analysis of the salts.

It has been supposed by some that the "aquo" salt is converted into the M_2RuCl_6OH by the action of concentrated hydrochloric acid, and in some of the earlier work in this Laboratory there seemed to be indication of this. To test this point, a particularly pure sample of $K_2Ru^{iii}Cl_6 \cdot H_2O$ was dissolved in dilute hydrochloric acid and twice evaporated on a hot-plate with concentrated hydrochloric acid to crystallization. The only crystals obtained were those of the original "aquo" salt, and the solution retained the color of the pure "aquo" salt. Later it was found that in cases where the quadrivalent salt had apparently been obtained from the trivalent salt by the action of hydrochloric acid, the latter salt had been originally contaminated by the quadrivalent salt owing to incomplete conversion by alcohol.

The difficulty of *complete* conversion of the salts of the three series, M_2RuCl_6 , $M_2Ru^{iv}Cl_6OH$ and $M_2Ru^{iii}Cl_6 \cdot H_2O$, into one another should be emphasized; it results in great difficulty in preparing pure salts for analysis, and is undoubtedly responsible for many irregularities in analytical figures.

The analyses were carried out, as usual, in this Laboratory, by heating the salt in a stream of purified and dried hydrogen and collecting the evolved hydrogen chloride in a solution of silver nitrate. The combustion tube was of Jena glass, one end drawn out somewhat, and so bent as to dip directly into the silver nitrate solution. It was heated in an electric combustion furnace with the top so hinged that the tube could be inspected, if desired, during heating. The salt was contained in a small boat of fused quartz. The precipitated silver chloride was collected and weighed in a Gooch filter and dried in an electric oven at 110° . Thus far the analysis gives, from the loss in weight in the boat, the $Ru + 2MCl$, and, from the weight of the silver chloride, the chlorine "connected with the ruthenium."²³ Any water or hydroxyl present will appear as loss. As already noted, Briggs has called attention to the fact that such a water determination is unreliable, since all the errors fall on the loss. This is brought out by an inspection of a large series of analyses, where the loss

²³ In most cases, the residue in the boat was treated with hot water, the ruthenium filtered, burned and reheated in hydrogen; the alkali chloride evaporated in a fused quartz crucible and weighed. Frequently, as Briggs has pointed out, a little of the alkali chloride is not dissolved out by a single extraction, and hence the ruthenium results are often a little high and those for the alkali chloride correspondingly low. A number of experiments showed that this error was generally less than 0.1%.

shows considerable variation. Further, of course, it does not discriminate between water and hydroxyl. For this reason, in a number of cases, the water from the hydroxyl group was determined directly by absorption in phosphorus pentoxide. As it was necessary to heat the salt to a fairly high temperature to insure the decomposition of the hydroxyl, the chlorine connected with the ruthenium was also evolved. In earlier work this chlorine was retained by passing over heated silver foil; more recently anhydrous sodium carbonate was used. The front of the combustion tube was filled for a distance of ten centimeters with recently heated, anhydrous sodium carbonate, and a layer of the same was placed over the salt in the combustion boat. Air was drawn through the tube by a suction pump, being dried by a calcium chloride tube and a phosphorus pentoxide tube before entering the combustion tube. The absorption phosphorus pentoxide tube was guarded by a calcium chloride tube and two sulfuric acid drying bottles, these serving also as a gage for the velocity of the air current. Several blanks were run before each series of analyses. The temperature used varied, in some cases being sufficiently high to fuse the sodium carbonate. This method was tested on $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and found to be accurate.

In considering the experimental work on each of the three series of chloro salts, the establishment of the formula has been first given, followed by the results of *all* the analyses made, as well as the origin of the salts, except in those cases in which there were evident analytical errors. It has been thought best to give all the analyses, in order that the material may be available to others who are working in this field and who may find some different interpretation.

Work on Series B; the Hexachloro-ruthenates, M_2RuCl_6

As these salts have already been well established as being formed by the action of chlorine on the "aquo" salts, it was further desirable only to determine whether they could also be formed by the action of concentrated hydrochloric acid on the pentachloro-hydroxy-ruthenates, thus confirming the constitution of the latter, and also to determine the amount of reduction in valence by the action of stannous chloride. The ordinary pentachloro-ruthenate (actually $\text{K}_2\text{RuCl}_5\text{OH}$) was recrystallized from concentrated hydrochloric acid. The crystals obtained resembled in every way those of the hexachloro-ruthenate, K_2RuCl_6 .

Anal. Calcd. chlorine removable by hydrogen: for K_2RuCl_6 , 36.13; for $\text{K}_2\text{RuCl}_5\text{OH}$, 28.43; for K_2RuCl_6 , 29.78. Found: 34.89.

It is probable that the conversion into the hexachloro salt was not complete; the analysis of a second crop of crystals, the hydrochloric acid having become less concentrated by evaporation, gave only 27.85% of chlorine, corresponding to the pentachloro-hydroxy salt.

Titration of the recrystallized salt with stannous chloride to the "aquo" salt: Theoretical for reduction of one valence, 25.89; for reduction to bivalent ruthenium, 12.94. Found: ruthenium (six titrations), 24.10 to 25.31%.

This established the fact that the hexachloro salt is formed from the pentachloro

salt by recrystallization from concentrated hydrochloric acid; hence, since oxidation under these conditions is out of the question, the valence of ruthenium in the pentachloro salt is the same as in the hexachloro salt, that is, *four*. From this standpoint the pentachloro salt is to be looked on as a one-fourth hydrolyzed hexachloro salt.

TABLE I

ANALYSES

	Calcd.	(23) ^a	(24) ^b	Antony ^c
Taken, g.		0.2336	0.2549	
Ru + 2KCl, %	63.87	64.82	64.69
Ru, %	25.89	25.912
2KCl, %	37.98	37.936
Cl ₄ , %	36.13	34.89	35.26	36.074
Cl ₅ , %	54.163	54.146

TITRATION WITH SnCl₂ TO PINK "AQUO" SOLUTION

	Calcd.	(23)	(23)	(23)	(23)	(24)	(24)
Taken, g.	...	0.0837	0.0853	0.1041	0.1033	0.0347	0.0835
Ru, %	25.89	25.31	24.47	23.42	24.27	23.91	24.64
	Calcd.	(24)	(24)	(24)	(24)	(25) ^a	(25)
Taken, g.	...	0.1066	0.1124	0.1083	0.1319	0.1379	0.1301
Ru, %	25.89	24.69	24.07	23.03	24.39	24.10	24.64

^a (23), (25): K₂RuCl₅OH recrystallized from concentrated hydrochloric acid.

^b (24). Precipitated from concentrated solution of the "aquo" salt by chlorine.

^c Antony's salt (Ref. 21) was prepared by the action of very dilute hydrochloric acid on a potassium ruthenate, K₂RuO₄, melt containing potassium chlorate, and concentrated in a vacuum in the cold. Under these conditions neither further reduction nor hydrolysis took place.

Work on Series C; the Pentachloro-hydroxy-ruthenates, M₂Ru^{iv}Cl₅OH

In establishing the constitution of these salts, the crucial point, aside from the ordinary analysis, is the determination of the water and of the change of valence by the action of stannous chloride or potassium iodide.

The Potassium Salt.—In the two most reliable preparations (8) and (10), second and third crop recrystallizations, we have, as regards water directly determined by absorption in phosphorus pentoxide, the following results.

Anal. Calcd. for K₂RuCl₅OH: H₂O, 2.40; for K₂RuCl₅.H₂O: H₂O, 4.54. Found: 2.79, 2.23.

Results obtained as regards valence, by reduction with stannous chloride to the "aquo" salt:

Theoretical for reduction of one valence, 27.18. Ruthenium (seven²⁴ titrations), 24.05 to 26.64 per cent. The "aquo" salt (trivalent ruthenium) gives no reduction.

In the reduction by potassium iodide, no satisfactory end-point could be obtained, but the results (given below) point also to a reduction of one valence.

The Rubidium and Cesium Salts, Rb₂RuCl₅OH and Cs₂RuCl₅OH.—No new direct determinations of water were made with these salts, and little reliance can be placed on the water analyses of the earlier work, though the existence of a monohydrate of the cesium salt and possibly of the rubidium salt is distinctly pointed out. These salts are too slightly soluble for titration work.

²⁴ Two titrations giving 20.12 and 19.89 are omitted here as the salt was evidently contaminated by "aquo" salt.

These results, and numerous other titration experiments with the free acid (given in the following paper) seem to leave no doubt but that the salts formed when RuO_4 is dissolved in hydrochloric acid and an alkali chloride added, contain quadrivalent ruthenium, and that, unless the acid is very concentrated, the formula of such salts is $\text{M}_2\text{RuCl}_4\text{OH}$. The same is probably true regarding the bromo salts, as they seem to resemble the chloro salts in every particular.

TABLE II

ANALYSES OF POTASSIUM PENTACHLORO-HYDROXY-RUTHENATE, $\text{K}_2\text{RuCl}_5\text{OH}$

	Calcd.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Taken, g.	...	0.3369	0.3194	0.3719	0.3074	0.2818	0.2606	0.2964	0.2819	0.271
Ru + 2KCl, %	67.03	68.82	68.99	68.73	68.44	68.18	69.07	68.35	68.11	67.70
Ru, %	27.18	27.68	27.90	27.75	27.88	28.03	28.36	27.80	...	27.12
2KCl, %	39.85	40.49	40.56	40.56	40.35	40.28	40.08	39.91	...	39.60
$\text{Cl}_5 + \text{OH}$, %	32.97	31.18	31.01	31.27	31.56	31.58	30.93	31.04	31.89	32.30
Cl_5 , %	28.43	28.35	28.38	28.82	28.97	27.82	27.14	28.82	27.85	30.35
OH (loss), %	4.54	2.85	2.62	2.48	2.74	3.76	3.79	2.82	4.04	1.95

Water determinations by phosphorus pentoxide absorption

	Calcd.	(5)	(6)	(6)	(6)	(7)	(8)	(10)	(6)	(1)	(3)
Taken, g.	...	0.2496	0.3610	0.3058	0.4802	0.3718	0.4190	0.3434	0.4839	0.3104	0.3124
H_2O , %	2.40	1.62	.89	2.00	1.24	1.05	1.53	2.79	2.23	2.12	2.11

Valence determination by reduction to rose ("aquo") $\text{K}_2\text{Ru}^{\text{III}}\text{Cl}_5\cdot\text{H}_2\text{O}$ solution^a

	Calcd.	(5)	(5)	(6)	(6)	(7)	(7)	(8)	(8)	(9)
Taken, g.	...	0.1023	0.1035	0.1038	0.1046	0.1034	0.1075	0.1092	0.1053	0.1068
Ru, %	27.18	24.68	24.05	20.12	19.89	25.68	25.68	25.54	24.84	26.64

Valence reduction^b

	(6)	(6)	(6)	(5)
Taken, g.	0.1053	0.1343	0.1512	0.0693
Valence reduction	.960	.854	.904	1.020

^a Reduction by stannous chloride, iodine-starch indicator; the figures found represent the percentage of ruthenium in the salt, assuming the ruthenium to be reduced one valence.

^b Reduction by KI and titration with $\text{Na}_2\text{S}_2\text{O}_3$ solution and starch indicator. No satisfactory end-point was obtained, and hence these figures can be looked on as only approximate. The results, however, point very clearly to a reduction of one valence, that is, from quadrivalent to trivalent ruthenium.

Origin of salts

(1), (2): Recrystallized salt; dissolved in hot, dilute hydrochloric acid and concentrated acid added to about 6 N; brilliant black crystals.

(3), (4): Crystallized out from mother liquor of (1) while evaporating on hot plate; similar to (1).

(5): Recrystallized from dilute hydrochloric acid; brown.

(6): Recrystallized from 6 N hydrochloric acid on hot plate; black crystals but probably contaminated by a little "aquo" salt.

(7): Solution of RuO_4 in rather strong hydrochloric acid precipitated hot by KCl solution; fine black powder with bluish tint.

(8): Recrystallized salt, second crop; about 5 N acid.

(9): Evaporated filtrate from K_2RuCl_5 formed by leading chlorine into solution of the "aquo" salt; strong hydrochloric acid; evidently contained some unhydrolyzed K_2RuCl_5 .

(10): Third crop from (8).

With the above may be compared the original analyses of the same salt by Claus,²⁵ and the analyses by Miolati and Tagiuri.⁸

TABLE III

Component, %	EARLIER ANALYSES				Miolati and Tagiuri	
	Theory	Claus				
Ru	27.18	28.48	28.96	28.91	27.11	...
2KCl	39.85	41.30	40.80	41.08	39.21	...
Cl ₂ + OH (loss)	32.97	30.22	30.24	30.04	30.01 ^a	32.73
Cl ₂	47.38	...	48.30	48.95

^a Miolati and Tagiuri determined the chlorine only by loss, which would include also the hydroxyl group.

TABLE IV

ANALYSES²⁶ OF RUBIDIUM PENTACHLORO-HYDROXY-RUTHENATE, Rb₂RuCl₅OH

	Calcd.	(12) ^a	(13) ^a	(14) ^b	(15) ^a	(16) ^a	(17) ^a
Taken, g.	...	0.3235	0.2925	0.2598	0.2480	0.2027	0.1809
Ru + 2RbCl, %	73.79	72.17
Ru, %	21.78	22.13	22.46	22.25	23.15	22.39	20.95
2RbCl, %	51.81	53.59	51.93	51.90	50.64	52.58	51.16
Cl ₂ + OH, %	26.41	27.83
Cl ₂ , %	22.78	22.90	22.42	23.37	23.01	23.09	21.75
OH (loss), %	3.63	2.26	3.18	2.08	6.08 (0.27 at 145°)
H ₂ O (P ₂ O ₅), %	1.93	2.66

^a Recrystallized salt.

^b From warm hydrochloric acid.

^c From hot dilute hydrochloric acid.

TABLE V

ANALYSES OF CESIUM PENTACHLORO-HYDROXY-RUTHENATE, Cs₂RuCl₅OH

	Calcd.	(18) ^a	(18) ^a	(18) ^a	(19) ^a	(18) ^a	(20) ^b	(21) ^c	(22) ^b
Taken, g.	...	0.2779	0.2676	0.5029	0.1927	0.2802	0.4019	0.7412	0.4019
Ru + 2CsCl, %	78.02	...	76.46	76.75	76.85	76.73
Ru, %	18.11	...	18.87	18.32	17.80	...	18.61
2CsCl, %	59.91	...	58.56	58.43	58.85
Cl ₂ + OH, %	21.98	...	23.50	23.24	23.14	23.27
Cl ₂ , %	18.94	19.22	19.13	19.16	20.03	19.13	19.11
OH (loss), %	3.04	...	4.37	4.08	3.11	4.14
H ₂ O (P ₂ O ₅), %	1.60	6.00	3.28

^a Crystallized from evaporated solutions of H₂RuCl₅OH and cesium chloride; about 5 N hydrochloric acid.

^b Recrystallized from dilute hydrochloric acid; earlier analyses.²⁶

^c Crystallized from hot solution of H₂RuCl₅OH and cesium chloride in dilute hydrochloric acid on cooling. The water of this analysis corresponds to a monohydrate, Cs₂RuCl₅OH·H₂O (theory, H₂O = 6.04). (Analysis (17) of the rubidium salts points in the same direction, though this salt lost only 0.27 at 145°.) As the solution was only weakly acid, it is not unlikely that such a salt may have crystallized out, but the amount of the salt was too small to make a complete analysis, and this evidence is too slender to establish the existence of a monohydrate.

²⁵ Ref. 1, p. 353.

²⁶ Only a single new analysis of this salt was made, but for the sake of completeness

Work on Series D; the Pentachloro-ruthenites, $M_2Ru^{III}Cl_5H_2O$ (the "Aquo" Series of Howe and Beta Series of Aoyama)

The Potassium Salt.—Briggs¹² considers this salt to have the formula $2K_2RuCl_5 \cdot 3H_2O$, basing his view on his determination of water by loss in two analyses and one determination of water by combustion in oxygen. The recorded analyses of this salt are given below.

TABLE VI

	ANALYSES RECORDED		(a) ⁴	(a) ⁴	(a) ⁴	(b) ¹²	(b) ¹²	(b) ¹²
	Calcd. for $K_2RuCl_5 \cdot H_2O$	Calcd. for $2K_2RuCl_5 \cdot 3H_2O$	0.3927 g.	0.4792 g.	0.4335 g.			
Ru, %	27.09	26.48	26.84	26.84	..	26.7	26.7	26.6
2KCl, %	39.75	38.82	39.30	40.27
Cl ₅ , %	28.35	27.68	27.78
H ₂ O, %	4.80	7.03	...	6.07 ^a	4.82 ^b	7.05 ^c	7.0 ^d	7.1 ^d
2K, %	20.85	20.36	20.3	20.4	20.2
5Cl, %	47.25	46.13	46.0	45.9	46.1

^a Loss between 140 and 180° (possible incipient decomposition).

^b Absorbed in phosphorus pentoxide (heated to decomposition in current of air).

^c By combustion and absorption in calcium chloride.

^d Loss.

Stannous chloride, even in excess, was found to have no action on this salt; 0.1785 g. of salt was titrated with 0.1 *N* stannous chloride; 0.14 cc. was used, equivalent to 0.81% of quadrivalent ruthenium, thus indicating the presence of a very small quantity of unreduced salt, as generally happens in the reduction by alcohol.

The Cesium Salt, $Cs_2RuCl_5 \cdot H_2O$.—Since the "aquo" salts are not easy to prepare in a state of assured purity, it was hoped to get better results with the cesium salt, which is less soluble. RuO_4 was dissolved in hydrochloric acid, and the diluted solution boiled with alcohol. This solution was then either treated with cesium chloride and evaporated to crystallization, or was first evaporated and precipitated by a solution of cesium chloride. At times the salt was recrystallized from hydrochloric acid of varying strengths, and again solutions of the salt were precipitated by alcohol. The salt was sometimes obtained as fine, rose prisms similar to the potassium salt; sometimes "whetstone" crystals were obtained, similar to uric acid, or these may have been possibly a variety of the rose prisms; the rose prisms were generally accompanied by minute spherules, often adhering to the prisms and of a paler color, or sometimes as a dark powder; in one case (38) a sample consisting almost entirely of rose prisms recrystallized as apparently pure spherules. When precipitated by alcohol the salt was generally obtained as a buff, felt-like mass which under high powers of the microscope seemed to be made up of very minute rose prisms. Efforts to separate different forms of crystals by fractional crystallization were unsuccessful. As will be seen from inspection of the analyses, there are frequently considerable variations, but none of these are large enough to indicate the presence of an impurity differing materially in composition. In particular, no evidence was found of any sesquihydrate, as postulated by Briggs. The water present in the salt could not have been greater than the loss after accounting for the Cl₅, Ru and 2CsCl directly weighed. This loss in no instance exceeded 3.76%, and averaged 3.02 (16 analyses); theory requires 3.20 for the monohydrate, and 4.73 for Briggs'

it is worth while to put the earlier analyses on record in this connection; the composition of the salt was at that time supposed to be $Rb_2Ru^{III}Cl_5 \cdot H_2O$. [Howe, *THIS JOURNAL*, 23, 786 (1901).]

formula for a sesquihydrate. The average of three water determinations by absorption in P_2O_5 is 3.35.

It would thus appear that the formula $Cs_2RuCl_5 \cdot H_2O$ is established, and it is probable that the general formula for the chloro-ruthenites is $M_2RuCl_5 \cdot H_2O$, in which the ruthenium has a valence of *three* and a coordination number of *six*.

TABLE VII
ANALYSES OF CESIUM PENTACHLORO-RUTHENITE, $Cs_2RuCl_5 \cdot H_2O$

	Calcd.	(a)	(b)	(26)	(27)	(28)	(29)	(30)	(31)	(32)
Taken, g.	...	0.1493	0.2636	0.2658	0.2728	0.2627	0.3215	0.2433	0.2498	0.2740
Ru + 2CsCl, %	77.90	77.20	75.95	77.46	79.35	77.60	77.74	77.81
Ru, %	18.07	17.88	18.25	17.95	17.85	18.16	17.29	19.19	18.09	18.31
2CsCl, %	59.82	60.15	59.45	59.39	58.05	59.44	62.05	58.36	59.53	59.88
Cl ₅ + H ₂ O, %	22.11	22.80	24.05	22.54	20.65	22.40	22.26	22.19
Cl ₅ , %	18.90	18.93	18.76	20.02	20.39	19.89	18.24	20.49	19.91	18.48
H ₂ O (loss), %	3.20	2.97	3.74	2.78	3.75	2.64	2.41	1.91	2.35	3.71
		(33)	(34)	(29)	(35)	(36)	(37)	(38)	(36)	(35)
Taken, g.	0.2676	0.2672	0.2557	0.2559	0.3466	0.2665	0.2327	0.2574	0.1623	0.2842
Ru + 2CsCl, %	77.77	77.62	78.38	77.80	77.32	77.71	77.74
Ru, %	18.57	18.23	17.34	18.29	18.32	18.07	19.90
2CsCl, %	59.68	59.99	61.11	59.44	59.06	59.51	57.80
Cl ₅ + H ₂ O, %	22.23	22.38	21.62	22.20	22.68	22.29	22.26
Cl ₅ , %	19.19	18.93	18.63	18.69	18.90	18.79	20.19
H ₂ O (loss), %	3.06	3.65	2.99	3.50	3.76	3.50	2.07
H ₂ O (P_2O_5), %	3.21	3.33	3.52

Origin of salts

(a): Precipitated by alcohol from blue solution (electrolytically reduced) of $RuCl_3$ which had spontaneously oxidized in presence of hydrochloric acid and cesium chloride; buff powder.²⁶

(b): From evaporation of a solution of Cs_2RuCl_5 containing alcohol; rose prisms.²⁶

(26): From cold conc. hydrochloric acid; fine brown powder; largely "whetstones."

(27): From cold conc. hydrochloric acid; largely minute rose prisms.

(28): From warm conc. hydrochloric acid; dark brown powder; mainly rose prisms.

(29): From hot conc. hydrochloric acid; dark buff; largely spherules with prisms.

(30): From hot conc. hydrochloric acid; buff; chiefly rose prisms.

(31): Precipitated by alcohol; fine buff powder; chiefly rose prisms.

(32), (34): Precipitated by alcohol; fine buff felt; minute rose prisms.

(33): Precipitated by alcohol; darker buff felt than (32) and (34); minute rose prisms.

(35): Solution of RuO_4 in hydrochloric acid diluted and boiled with alcohol until color lightened, cesium chloride added, evaporated and cooled; fourth crop of crystals; almost pure rose prisms.

(36): Same, third crop; rose prisms with very small amount of dark powder.

(37): Same, first crop; rose prisms (?) in whetstone form.

(38): From solution of rose prisms containing some spherules; alcohol added and evaporated on warm plate in vacuum; apparently pure spherules. It may be noted that salts (29) and (38), both consisting largely of spherules, vary rather widely in analysis from theory, but in opposite directions.

Summary

The work described in this paper indicates that there is no isomerism among the known complex chlorides of ruthenium; that what has been

considered the series $M_2Ru^{III}Cl_6$ containing trivalent ruthenium, in reality contains quadrivalent ruthenium, of formula $M_2Ru^{IV}Cl_6OH$; that what has been considered an "aquo" series is actually the ordinary series of trivalent ruthenium, but always crystallizing as a monohydrate of formula $M_2Ru^{III}Cl_6 \cdot H_2O$. In all of these salts the coordination number of ruthenium is six. Also Claus' view that the blue solution of reduced ruthenium contains the metal in bivalent form is again confirmed.

LEXINGTON, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM. XI A VOLUMETRIC ESTIMATION OF RUTHENIUM

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The estimation of ruthenium, except in crystallized compounds, has always been difficult. Neither hydrogen sulfide nor metals, as zinc or magnesium, precipitate ruthenium completely from any of its solutions, and while it can be precipitated by caustic alkalies, it is impossible to wash the gelatinous precipitate free from salts. Somewhat more than a year ago it was found in this Laboratory¹ that ruthenium in a finely divided form could be completely dissolved in alkaline sodium hypochlorite solution and the ruthenium distilled quantitatively from this solution as ruthenium tetroxide after treatment with a stream of chlorine; but no simple method was found by which the ruthenium in the distillate could be estimated.

The reduction of quadrivalent ruthenium by stannous chloride, as described in the preceding paper, affords a solution of the problem. The volatile ruthenium tetroxide is condensed in concentrated hydrochloric acid, preferably in a small Erlenmeyer flask surrounded by ice. A two-necked Wolff bottle with ground-glass joints may be used if the amount of ruthenium is considerable, but with small quantities (as is usual in the analysis of alloys) we have found no difficulty in condensing all the RuO_4 in an Erlenmeyer flask. After all the ruthenium tetroxide has been reduced by the hydrochloric acid, which is apparent by the disappearance of any drops of liquid ruthenium tetroxide, the solution is boiled until all absorbed chlorine has been eliminated. It is then titrated with a solution of stannous chloride of about 0.05 *N* strength. The stannous chloride solution is standardized immediately before using against 0.1 *N* iodine solution with starch indicator.

In titrating the ruthenium solution, the stannous chloride can be added until the dark, brownish-red solution of quadrivalent ruthenium changes to the light red or rose of trivalent ruthenium. As this end-point is often

¹ Howe and Mercer, *THIS JOURNAL*, 47, 2926 (1925).

not sharp, it is better to use a slight excess of stannous chloride, add starch paste and titrate back with iodine solution. Since the ruthenium of ruthenium tetroxide is reduced only four units by hydrochloric acid, it does not matter whether the hexa- or the pentachloro salt is formed, as both contain quadrivalent ruthenium.² This titration was carried out in concentrated hydrochloric acid, as well as in quite dilute solutions; in hot solutions and in cold solutions; by adding only just sufficient excess of stannous chloride to make an iodine-starch reaction visible, and by adding a large excess of stannous chloride; in no case was there any evidence of conditions of titration making any difference in the results. Titrations of K_2RuCl_6 and of K_2RuCl_5OH gave the same results, as described in the previous paper. Reduction does not go beyond the rose trivalent ruthenium, as was shown by adding a large excess of stannous chloride solution and allowing it to stand for several days. No change was apparent in the solution, nor in any case was there any sign of blue or green, which would have indicated the presence of bivalent ruthenium.

It should be noted that in almost every case the amount of stannous chloride required for reduction was somewhat lower than that called for by theory. Just why this is, is not apparent.³ For this reason, the method cannot be recommended for accurate determination of ruthenium, but it affords a ready method for the approximate evaluation of ruthenium solutions, and also for the determination of ruthenium where only a small amount is present.

Experimental Work

A solution of ruthenium tetroxide in hydrochloric acid was prepared, containing 4.91 mg. of ruthenium per cc., as determined by the evaporation of 10 cc. in a quartz boat, heating in the air and reducing in hydrogen. The ruthenium was reoxidized and reduced without change in weight. Two cc. portions of this solution were then titrated with stannous chloride solutions, varying from 0.08 to 0.03 *N*. As this solution was used as a check in titrating the chlororuthenate salts, it was actually titrated many times. The results, omitting only three which were manifestly in error, are as follows.

TABLE I

RUTHENIUM FOUND, MG. PER CC. IN TEST SOLUTION CONTAINING 4.91 MG.

4.81, 4.58, 4.60, 4.93, 4.98 (excess $SnCl_2$), 4.72, 4.62, 4.81 (in concd. HCl), 4.60, 4.82, 4.82 (very dilute HCl), 5.05, 4.65, 4.94 (warm), 4.75, 4.68, 4.85, 4.82, 4.74 (excess $SnCl_2$ in concd. HCl , hot); average of 19 titrations, 4.766.

² Howe, *THIS JOURNAL*, 49, 2381 (1927).

³ It is possible that it may have been due to the small quantities used, and that the results might have been made to approach the theoretical more closely by using large amounts, or by titrating with more dilute solutions. A more probable explanation is that there was a small quantity of trivalent ruthenium present, which would not be recognized as such by gravimetric analysis, but would affect the volumetric analysis.

TABLE I (Concluded)

RUTHENIUM FOUND IN K_2RuCl_6 ; ⁴ THEORETICAL, 25.89%

22.65, 23.91, 23.03, 24.10, 22.11, 24.64, 24.39, 24.64, 25.31, 24.69, 23.42, 24.47, 24.07, 24.27; average of 14 determinations, 23.99.

RUTHENIUM FOUND IN K_2RuCl_6OH ; THEORETICAL, 27.18%

24.675, 25.68, 26.64, 24.05, 25.68, 20.12, 25.54, 19.89, 24.84; average of 9 determinations 24.124.

Summary

This paper presents a simple method of determining ruthenium volumetrically, when present in small amounts, and of evaluating ruthenium solutions approximately.

LEXINGTON, VIRGINIA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 41]

AN INVESTIGATION OF THE REACTION OF ALUMINUM WITH THE AMMONIUM SALT OF AURINTRICARBOXYLIC ACID UNDER DIFFERENT EXPERIMENTAL CONDITIONS, AND ITS APPLICATION TO THE COLORIMETRIC DETERMINATION OF ALUMINUM IN WATER

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Recently Hammett and Sottery¹ described a new qualitative test for aluminum in which the principal reagent is the ammonium salt of aurintricarboxylic acid, now sold under the trade name, "Aluminon." These authors studied the behavior of several of the elements and ions commonly dealt with in qualitative analysis which would be likely to interfere with the test. Middleton² and later Corey and Rogers³ have studied the behavior of several of the less common elements with "Aluminon." A brief summary of the results with respect to the final solution follows.

1. Silicic acid, salts of antimony, bismuth, lead, mercuric mercury, stannic tin and titanium give white precipitates. The qualitative test may be made without a separation.

2. Salts of cadmium, chromium, cobalt, germanium, indium, manganese, nickel, rare earths, thallium, thorium, zinc and zirconium give no precipitates.

3. Ferric salts produce a reddish-brown precipitate which is stable under the same conditions as the aluminum lake. Beryllium gives a lake which cannot be distinguished from aluminum. The gallium lake

⁴ For details see ref. 2.

¹ Hammett and Sottery, *THIS JOURNAL*, **47**, 142 (1925).

² Middleton, *ibid.*, **48**, 2125 (1926).

³ Corey and Rogers, *ibid.*, **49**, 216 (1927).

dissolves with difficulty in 2 *N* ammonium carbonate, leaving a red-colored solution.

4. Phosphates tend to prevent the formation of the lake, and reducing agents such as hydrogen sulfide, sulfur dioxide, etc., destroy the color.

Lundell and Knowles⁴ adopted the "Aluminon" reagent in preference to sodium alizarin sulfonate⁵ since "it requires less time and is more sensitive, particularly in the presence of precipitates such as stannic hydroxide." They found that the final color is unsatisfactory when the ammonium hydroxide-carbonate solution is added too rapidly, or in large excess; also when the amount of aluminum is very small and proportionately large amounts of precipitates are present.

A further investigation seemed well worth while, having for its purpose the study of the effects of changing the several factors in order to determine the optimum conditions for the reaction, with a view towards making a more general application in the field of quantitative analysis.

Apparatus and Reagents

The dark-room consisted of a wooden box of convenient dimensions mounted on a table. The inside of the box was painted a dull black and a curtain of heavy black cloth covered the open side and extended almost to the floor. The source of light was a Bausch and Lomb daylight lamp which was supported on a platform rigidly attached to the wall of the box. The legs of the lamp fitted snugly into holes in the platform and the source of light was thus kept in one position throughout the course of the work. Three strips of wood were screwed to the floor of the box in such a manner that they served as guides for placing the colorimeter always in the same position with respect to the lamp. A colorimeter of the Kennicott-Campbell-Hurley type was employed.

Carefully matched Nessler tubes of 50cc. capacity were employed, the dimensions of the tubes being those established by the American Public Health Association. The tubes were also marked to indicate a volume of 30 cc. The reagents were measured out with precision pipets of the desired capacity. The pipets were labeled so that a given pipet was always used for one solution only, and where necessary these were calibrated.

The purest chemicals obtainable were used in the preparation of the reagents, and the solutions were stored in the dark in Pyrex flasks which were carefully cleaned and steamed out just before being filled. Comparison solutions to which aluminum had not been added gave as a final color the characteristic yellow of the dye.

Reagents

1. Hydrochloric acid, 1 *N* and 4 *N*. 2. Nitric acid, 5 *N*. 3. Ammonium hydroxide, 5 *N*. 4. Ammonium hydroxide-carbonate solution; 250 g. of ammonium carbonate dissolved in a liter of 6 *N* ammonium hydroxide. 5. Ammonium carbonate solution, 5 *N*. 6. Sodium hydroxide solution, 6 *N*. 7. Ammonium acetate solution, 3 *N*. 8. Standard aluminum chloride solution; 8.952 g. of pure aluminum chloride hexahydrate⁶ dissolved in distilled water and diluted to a liter. The mean of three

⁴ Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

⁵ Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).

⁶ Dennis, *Z. anorg. Chem.*, **9**, 839 (1895); also, J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, p. 315.

closely agreeing analyses, carried out according to the method of Blum,⁷ showed that 1 cc. contained 0.999 mg. of aluminum. Ten cc. of this stock solution was diluted to a liter and mixed thoroughly. One cc. of the dilute solution contained 0.010 mg. of aluminum. 9. Solutions of the several salts which were used in studying the effects of ions were prepared so that 1 cc. would contain 10 mg. of the desired ion if the salt were completely dissociated. In the study of positive ions, chlorides or nitrates were used; in all other cases sodium salts were employed. 10. "Aluminon" reagent, 0.1% solution in water. The salt was obtained from the Fales Chemical Co., 74 Cortlandt St., New York City. 11. "Aluminon" reagent, 0.2% solution in water. 12. Methyl red, 0.05% solution in water. 13. Neutral litmus paper. 14. Starch solution, 1%. One gram of potato starch boiled in 100 cc. of distilled water for three hours, water being added from time to time to keep the volume at 100 cc. Transferred while hot to a sterilized, glass-stoppered bottle, and after allowing it to settle the clear supernatant liquid was pipetted out as needed.

Experimental

The order of addition of the reagents, as well as the quantities added, unless otherwise stated, was as follows. To the stated amount of aluminum in a Nessler tube were added 5 cc. of 1 *N* hydrochloric acid, 5 cc. of 3 *N* ammonium acetate and sufficient distilled water to bring the volume to the 30cc. mark. Then 5 cc. of the "Aluminon" reagent was added and the solution mixed thoroughly. It was allowed to stand for five minutes, reckoning the time from the beginning of the addition of the "Aluminon" to the beginning of the addition of the ammonium hydroxide, and 2 cc. of 5 *N* ammonium hydroxide and 10 cc. of 5 *N* ammonium carbonate were added slowly with constant stirring. The solution was diluted to 50 cc., mixed thoroughly and transferred to the colorimeter tubes just before comparison.

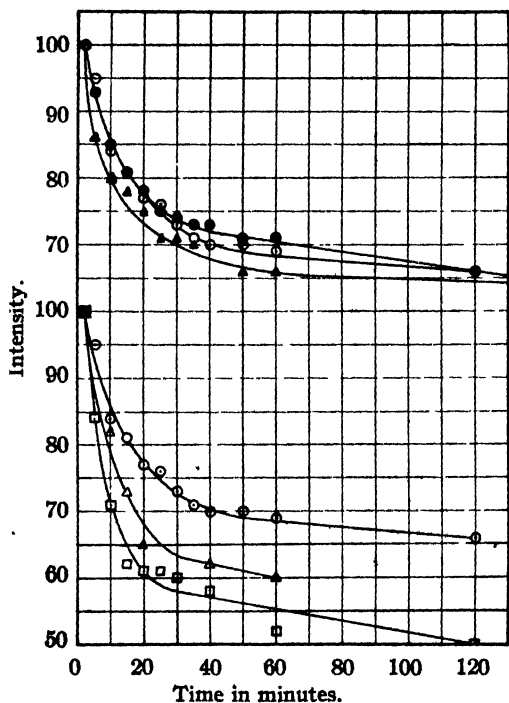
The measurements were carried out in such a manner that sufficient time was given for the operator's eyes to become adjusted to the dark before the readings were taken. Two "settings" of the colorimeter were made, one being made as the height of the adjustable column was increased, the other as its height was decreased. In order to obtain the best average value, the first reading was taken a few seconds before the end of the time interval and the second a few seconds afterwards. From the mean of the two readings the intensity was calculated by expressing the mean of the readings at the end of a given time interval as a percentage of the mean of the readings at the end of two minutes, the latter being considered as having an intensity of 100%. Beginning with the measurements on varying quantities of the reagents, the mean of the readings at the end of twenty-five minutes was adopted as the value corresponding to an intensity of 100%.

During the course of the earlier measurements a new standard was prepared for each comparison. However, it was found that considerable time could be saved by preparing a standard solution of the desired strength and allowing it to stand for several hours. After this period the rate of change of color intensity is small, and without appreciable error from this source a whole series of measurements could be made against the same standard. In order to obtain the reading corresponding to an intensity of 100%, 50 cc. of a fresh solution was prepared and allowed to stand for two minutes or twenty-five minutes, depending upon whether the results were to be expressed in terms of the intensity at the end of two minutes or that at the end of twenty-five minutes. At the end of this time the fresh standard was compared with the solution which had stood for several hours, the height of the column of the latter being taken as the reading

⁷ Blum, *THIS JOURNAL*, 38, 1282 (1916); also *Sci. Paper* No. 286, U. S. Bureau of Standards, 1916.

corresponding to an intensity of 100%. A similar comparison was made at the beginning of each series of measurements.

"Aging."—The decrease in color intensity with time after the addition of ammonium hydroxide, or "aging," was studied both in the light and in the dark. In both cases the solutions were allowed to stand in the colorimeter; in the former the colorimeter was removed from the dark room after each reading and placed in the diffused light of a well-lighted laboratory, while in the latter the colorimeter was left in the dark



○ 2 cc. NH_4OH in light; □ 5 cc. NH_4OH in light; ● 2 cc. NH_4OH in dark; ▲ 0.2% "Aluminon" in dark; △ 2 cc. $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$ in light.

Fig. 1.—"Aging."

of 0.1% solution, and when the ammonium hydroxide-carbonate reagent was used.

Effect of Varying the Quantities of the Reagents.—The quantities of the reagents were varied one at a time, all other conditions being kept constant. In each instance the temperature was 23° . All solutions were "aged" for 25 minutes and the intensity is given in terms of the intensity of the standard at the end of 25 minutes. The results are shown in Figs. 2 and 3.

Conditions During Lake Formation.—Three variable conditions were

room. The results are shown in Fig. 1. The results for two concentrations of ammonium hydroxide are given. When 1 cc. of ammonium hydroxide was added in the neutralization, in which case the final solution was just neutral to litmus paper, the color intensity was about 20% higher than when 2 cc. was used. For higher concentrations of ammonium hydroxide, Fig. 3 may be studied. Measurements were made on solutions containing different aluminum concentrations. The results were identical, and, unless otherwise stated, an aluminum content of 0.1 mg. has been adopted as the standard in all measurements. For comparison, curves are shown in Fig. 1 for "aging" when 0.2% "Aluminon" solution was employed instead

studied, namely, (1) the time allowed for the lake to form, (2) the temperature at which the lake was formed and (3) the volume of the solution at the time the lake was formed. In (2), Nessler tubes containing the mixture of aluminum, hydrochloric acid and ammonium acetate solutions were permitted to stand in a water-bath for ten minutes before the addition

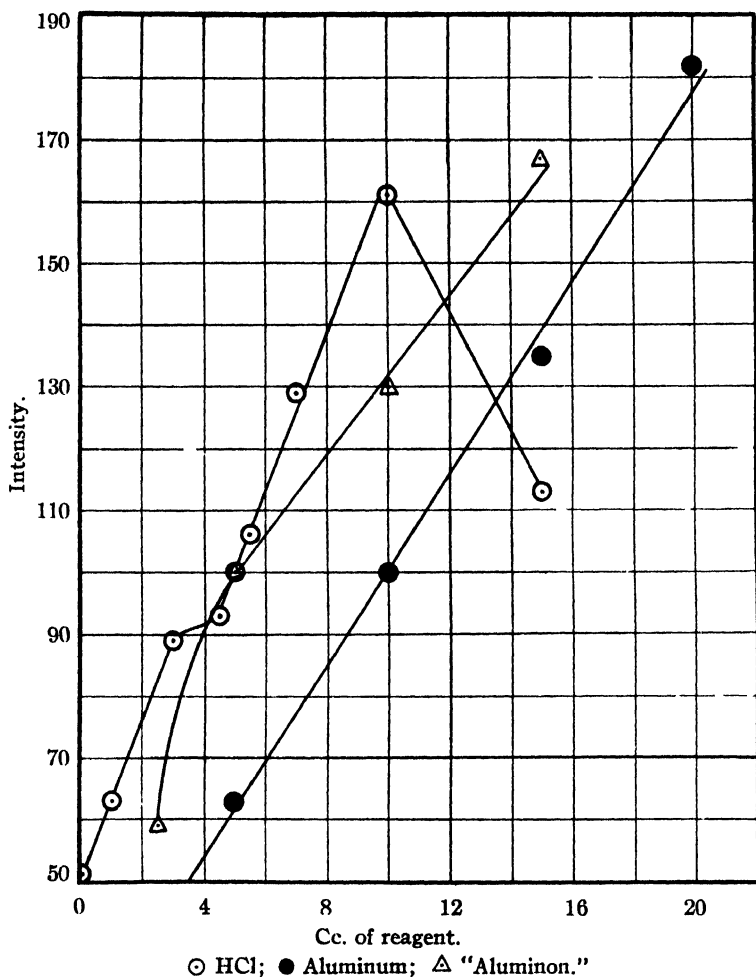


Fig. 2.—Variation in quantities of reagents.

of the dye, which was also at the temperature of the bath. Upon the addition of the ammonium hydroxide, the Nessler tubes were removed from the bath and placed in the rack until time for comparison. The results are shown in Figs. 4 and 5.

Presence of Other Ions.—The stated quantities of the ions were added to Nessler tubes containing 0.1 mg. of aluminum just before the

addition of the hydrochloric acid. The intensity of solutions containing 150 mg. of iodide, nitrate, nitrite and sulfate ions, respectively, was sensibly the same as that of the standard containing only aluminum. The effects

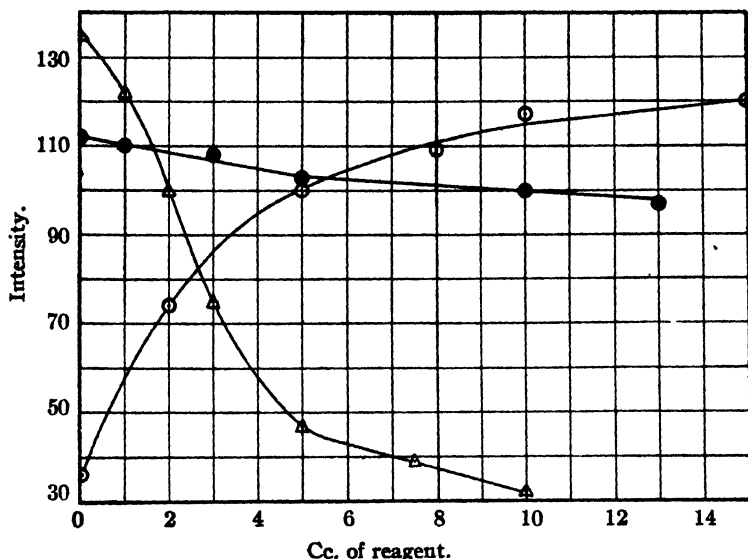


Fig. 3.—Variation in quantities of reagents. ○ NH₄Ac; ● (NH₄)₂CO₃; △ NH₄OH.

of the orthophosphate ion and silica are shown graphically in Fig. 6, while that for iron is given in Table I. The intensity of the solution containing 0.01 mg. each of iron and aluminum was too weak for com-

TABLE I
EFFECT OF IRON ON THE COLOR INTENSITY

Mg. of iron	Mg. of aluminum	Intensity
0.00	0.10	100
.01	.10	100
.03	.10	121
.01	.01	?

TABLE II
EFFECT OF CERTAIN COMMON IONS ON THE COLOR INTENSITY

Ion	Intensity 1 mg. of ion	Intensity 10 mg. of ion
Cu ⁺⁺	100	...
CrO ₄ ⁻⁻	112	Too intense for comparison
Co ⁺⁺	110	Too intense for comparison
Mn ⁺⁺	117	Very turbid
Ni ⁺⁺	108	138
Ca ⁺⁺	102	Very turbid
Mg ⁺⁺	102	115
PO ₄ ⁻⁻⁻	(5 mg.) 107 (turbid)	Very turbid

parison in the colorimeter but comparison in the Nessler tubes showed a distinct difference. An attempt was made to prevent the iron lake from forming by the addition of citric acid, with the result that neither the iron nor the aluminum lake was formed in its presence. The results for several other ions which were studied in less detail are shown in Table II. The presence of 0.01 mg. of sulfur as sodium sulfide did not alter the intensity appreciably, but with 0.1 mg. present the intensity was reduced to 94.

Limits of the Test for Colorimetric Work.—With 0.001 mg. of aluminum in a 50cc. Nessler tube the color could not be distinguished from that of a "blank" which contained no aluminum. A faint pink was perceptible when 0.002 mg. of aluminum was present. The lake did not settle out with 0.5 mg. of aluminum present but the solution was too highly colored

for comparison with the colorimeter employed in this work. With 1 mg. of aluminum a slight coagulation was observed after one hour, with 3 mg. the lake had coagulated at the end of ten minutes, and with 5 mg. the coagulated lake had begun to settle at the end of ten minutes. In these

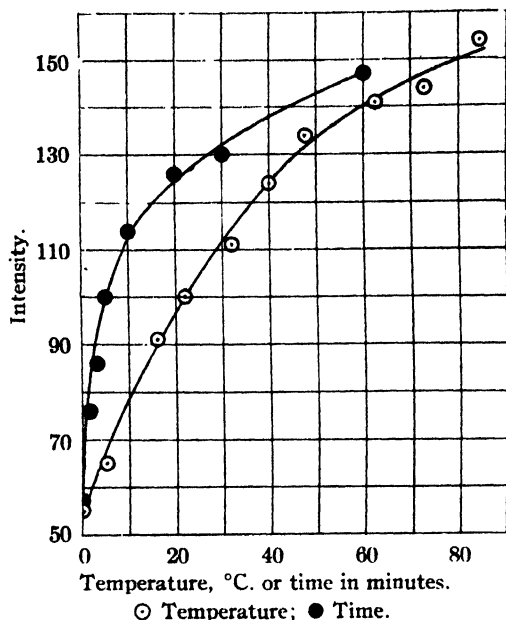


Fig. 4.—Time for lake formation and temperature.

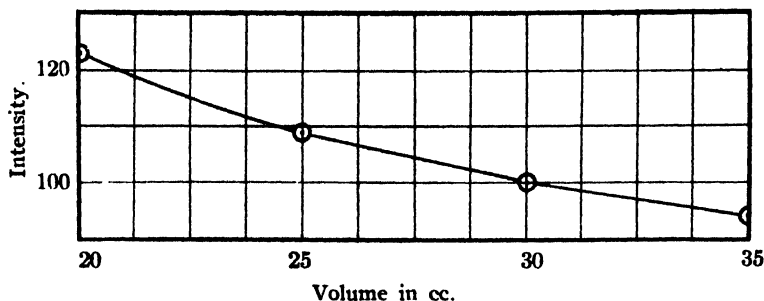


Fig. 5.—Variation in volume at lake formation.

experiments 2 cc. of ammonium hydroxide was added. An increase in the quantity of alkali hastened the process of coagulation.

A few observations were made on the effect of adding starch as a pro-

TECTIVE COLLOID just before the addition of the ammonium hydroxide, with a view towards stabilizing the lake with the higher concentrations of aluminum. The results for 3 mg. of aluminum are summarized below.

Time in minutes	No starch added	1% starch solution added	
		5 cc.	10 cc.
10	Coagulated	Suspended	Suspended
20	Settled	Began coagulating	Suspended
180	Signs of coagulation

The effect of starch on the stability of the color intensity was determined using 0.1 mg. of aluminum.

Cc. of 1% starch solution added.....	0.00	0.5	1.0	5.0	10.0
Intensity of color after 25 minutes....	100	106	106	100	82

In the determination of the "sensitiveness" of the test, the experimental method of Horn and Blake⁸ was used. A series of five solutions was

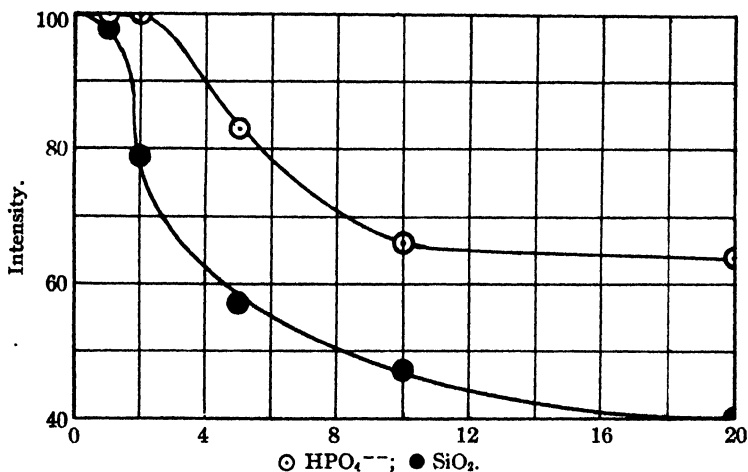


Fig. 6.—Orthophosphate ion and silica.

prepared in marked Nessler tubes of 50cc. capacity, such that the aluminum content of each solution differed from the one immediately before it in the series by a constant amount, the concentration of aluminum in the third solution being that at which the sensitiveness was to be determined. After standing for 25 minutes the tubes were arranged out of their regular order, and four men, separately and unaided, attempted to rearrange them in their proper order. Several such sets of tubes were prepared in which the difference in aluminum content was constant for a given set, though differing from series to series, until finally a series was obtained which could barely be rearranged with certainty by four different persons. The aluminum increment in this series was taken as the amount

⁸ Horn and Blake, *Am. Chem. J.*, 36, 195 (1906).

of aluminum necessary to produce a difference in the color intensity barely perceptible with certainty at the concentration of the third tube in the series. According to Horn's definition, the reciprocal of this increment in milligrams is the sensitiveness at the given concentration. This procedure was repeated at several concentrations. The results are shown in Table III, in which, according to the nomenclature of Horn, V is the volume in liters of the solution which contains one gram atom of aluminum; B is the milligrams of aluminum in 50 cc. of the solution; Δ is the amount of aluminum in milligrams necessary to produce a perceptible difference in the intensity of 50 cc. of a solution containing B mg. of aluminum; S is the sensitivity and equal to the reciprocal of Δ and $B' = B + \Delta$. The sensitivity curve for aluminum is shown in Fig. 7, in which the square roots of V and S have been employed for convenience in plotting.

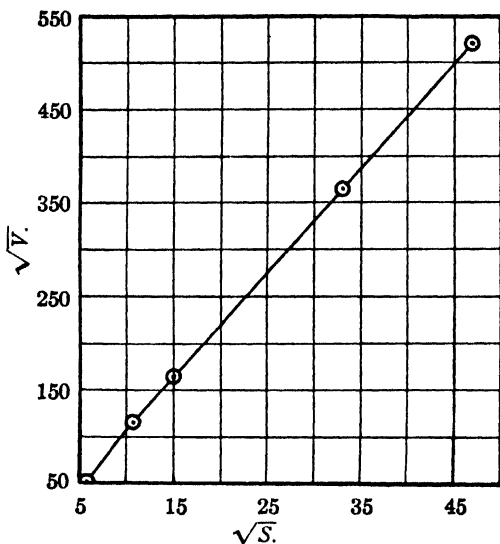


Fig. 7.—Sensitivity curve.

TABLE III
SENSITIVENESS

V	B	Δ	S	B'	Δ/B'	\sqrt{V}	\sqrt{S}
1,355	1.000	Too intense for determination					
2,710	0.500	0.025	40	0.525	0.048	52	6.3
13,550	.100	.009	111	.109	.083	116	10.6
27,000	.050	.0045	222	.0545	.083	165	15.0
135,000	.010	.0009	1111	.0109	.083	365	33.2
271,000	.005	.00045	2220	.00545	.083	520	47.0
1,355,000	.001	Matched solution to which no aluminum had been added					

Determination of Aluminum in Water.—Four samples of water of different iron content were analyzed for aluminum by the three methods described below. The results in parts per million are given in Table IV.

1. The aluminum was determined gravimetrically according to the method given in "Standard Methods of Water Analysis," American Public Health Association, 6th ed., New York, 1925, except that the hydroxides of aluminum and iron were precipitated by adding 5 *N* ammonium hydroxide until the solution was just neutral to methyl red. The iron was determined colorimetrically by the thiocyanate method.

2. A direct determination of the aluminum was made using "Aluminon;" 100–200

cc. of the sample, after the addition of 1-2 cc. of 4 *N* hydrochloric acid, was evaporated to dryness on the water-bath, and the residue ignited at dull redness for a few minutes to destroy any organic matter. After cooling, the ignited residue was taken up with a few drops of 4 *N* hydrochloric acid and 5 cc. of hot water and filtered in order to remove the small amount of silica which had separated. After washing the filter three times with small portions of hot water, the combined filtrate with washings was made neutral to litmus paper by adding 4 *N* hydrochloric acid and transferred to a 50cc. Nessler tube. After the addition of 5 cc. of 1 *N* hydrochloric acid, 5 cc. of 3 *N* ammonium acetate and sufficient distilled water to bring the volume to 30 cc., 5 cc. of 0.1% "Aluminon" solution was added and mixed. When the solution had stood for five minutes, 5 cc. of 5 *N* ammonium hydroxide and 10 cc. of 5 *N* ammonium carbonate were added slowly with constant stirring. The solution was now diluted to 50 cc. and mixed, and after standing for twenty minutes it was compared against standard aluminum solutions in Nessler tubes which were prepared and "aged" in a similar manner. In order to correct for the iron, a quantity of iron equivalent to that found in (1) was added to the standard.

3. In this case the aluminum was separated from the iron. A 300-550cc. sample of the water was treated as stated in (1) above until the precipitates of aluminum and iron hydroxides were filtered the first time. This precipitate was dissolved in 5 cc. of warm 5 *N* nitric acid by pouring the acid through the filter three times, and finally washing the filter three times with small quantities of hot water. The combined filtrate with washings was evaporated on the hot-plate to 1 cc., made strongly alkaline with 6 *N* sodium hydroxide, brought to boiling and filtered through a very small filter paper. The filter was washed three times with small quantities of hot water, and the filtrate with washings, after being made neutral to litmus paper by the addition of hydrochloric acid, was transferred to Nessler tubes and cooled. The procedure was completed from this point in (2) above.

TABLE IV
DETERMINATION OF ALUMINUM IN WATER

Sample	Iron (p.p.m.)	Aluminum (p.p.m.)		
		Method 1, gravimetric	Method 2, direct detn.	Method 3, separation of Fe
I	0.00	0.05	0.05	0.05
II	.66	1.03	.22	1.09
III	.23	0.51	.10	0.41
IV	5.00	.59	.12	.62

Discussion

The results for "aging" with 2 cc. of ammonium hydroxide, where the solutions were "aged" in the light and dark, respectively, are represented graphically in Fig. 1. There is little difference at any time between the intensities in the two cases. Although the curves diverge from each other in the manner which is to be expected if light has an appreciable effect on the stability of the color, the maximum difference of about 2% is within the limits of the experimental error. Thus, the rate of decrease in intensity appears to be independent of the diffused light of the laboratory.

The lower curves in Fig. 1 show the effect of the concentration of the ammonium hydroxide. Here, as in each case studied, the period of "aging" may be divided into two parts according to whether the slope

of the curve is "steep" or "flat." With the addition of ammonium hydroxide a comparatively short interval begins, in which the rate of decrease in intensity is very rapid. This period merges into the second and comparatively long period of slow change in intensity. With 2 cc. of ammonium hydroxide the first stage is 35 minutes long, while with 5 cc. this time is almost halved; however, in the latter instance the intensity is decreased by about 15% in the second period.

In Figs. 2 and 3 are shown the effects of varying the quantities of the reagents. The intensity increases with the concentration of hydrochloric acid to a maximum value, then drops rapidly on a further increase in the acid concentration. With an increase in the quantity of ammonium hydroxide, the intensity decreases along a curve which is very similar to the curves for "aging." The effect of ammonium carbonate is least of all, being a decrease in intensity of about 15% for 13 cc. of the reagent. In the case of the other three reagents the intensity increases with the concentration.

For the colorimetric determination of aluminum with "Aluminon" a procedure has been given which is in accord with the facts brought out in the foregoing curves. The quantities of the reagents, the time given for lake formation and all other conditions have been chosen, where possible, so that slight variations in the several factors will produce a minimum effect on the final color intensity and, therefore, a minimum error in the determination. Since the test is fairly sensitive to a change in the acid concentration, the solution to be examined for aluminum must be neutral at the time the hydrochloric acid is added. Furthermore, since the curves for the change in intensity with temperature and the time at lake formation are quite steep, it is obvious that the unknown solution and the standards must be at the same temperature during lake formation, and that the time intervals must also be of equal length. Where the analyst has the time, something in accuracy may be gained by giving a longer period for the lake to form.

Certain substances interfere with the test, and in this connection the effect of several ions likely to be encountered in water analysis has been studied. One mg. of silica or 2 mg. of HPO_4^{--} may be present without the results being impaired. While the orthophosphate ion tends to give low results by preventing the formation of the aluminum lake, the normal phosphate ion causes a turbidity which tends towards high results. Similarly, calcium and manganese produce turbid solutions. Some numerical values for the permissible quantities per 50 cc. of solution are given in Table II.

The results in Table I seem to indicate that iron may be present with aluminum in the ratio of 1:10 without vitiating the results. However, if as much as a few hundredths of a milligram of iron is present, a separa-

tion is necessary regardless of the ratio, since the combined iron and aluminum lakes will give a solution which is too deeply colored for accurate comparison. A fairly rapid procedure for the separation of iron from aluminum has been described with which results have been obtained by the "Aluminon" method for several samples of water that agree closely with the values for the aluminum content found by the longer and more tedious gravimetric method.

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	CrO_4^{--}	Cu^{++}	$[\text{Cu}(\text{NH}_3)_4]^{++}$	Aluminum-lake
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^a Calculated from Horn's data, Ref. 9.

Summary

An experimental study of the new reagent for aluminum, the ammonium salt of aurintricarboxylic acid, has been made and quantitative measurements of the effects of the following variables were obtained: (1) time, (2) temperature, (3) volume, (4) concentration of reagents and (5) the presence of other ions.

The range of the test has been determined for colorimetric work and a means of extending the range so as to include higher aluminum concentrations has been found. The sensitiveness of the test has also been determined.

Based upon the results of the experimental study, a quantitative method for the colorimetric determination of aluminum by the ammonium salt of aurintricarboxylic acid has been developed and applied to the direct determination of aluminum in potable water.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. III THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN CARBON TETRACHLORIDE SOLUTION

BY IGNACE J. KRCHMA AND JOHN WARREN WILLIAMS

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In the preceding paper of this series,¹ as well as in a number of other articles,^{2,3,4} it has been shown that the concept of molar polarization introduced by Debye⁵ has made possible a treatment of dielectric constant and density data for certain binary liquid mixtures such that the electric moments of the solute molecules can be calculated provided they are dissolved in a medium which has no electric moment itself. It was stated¹ that liquids such as carbon tetrachloride, carbon bisulfide, pentane, hexane and benzene should act as suitable solvents of this type. The purpose of this paper is to present the results of calculations of the electric moments of certain organic molecules from measurements of the dielectric constants and the densities of their solutions in carbon tetrachloride. The mathematical expressions necessary for this calculation were presented in the previous paper and will not be repeated here.

Method

Two distinct methods were used for the determination of the dielectric constants of the binary mixtures. The first, an electrical resonance method, was described in some detail in the first paper of this series.⁶ The second was one of the so-called bridge methods. It was necessary to use this second method for certain of the binary mixtures since a resonance method of the type referred to above fails for liquids which have any appreciable electrical conductance.

Since the bridge as set up contains several novel features it will be briefly described. It is shown diagrammatically in Fig. 1. The instantaneous potential of an alternating current for any given instant is determined by the "phase angle" obtained in a vectorial consideration of the inductance and capacitance. The phase angle of the current at the point "a" must equal the phase angle of the current at "b" in order that the points "a" and "b" be at equal potential at all times and that no current be detectable in "G." Since the phase angle is dependent on the resistance, inductance and capacitance in the arms, then in this sort of bridge a balance of resistance and inductance is required along with a balance of capacitance.

¹ Williams and Krchma, *THIS JOURNAL*, 49, 1676 (1927).

² Lange, *Z. Physik*, 33, 169 (1925).

³ Debye, "Handbuch der Radiologie" (Marx), 6, 625 (1925).

⁴ Smyth, *THIS JOURNAL*, 49, 1030 (1927).

⁵ Debye, *Phys. Z.*, 13, 97 (1912); *Verhandl. deut. phys. Ges.*, 15, 777 (1913).

⁶ Williams and Krchma, *THIS JOURNAL*, 48, 1888 (1926).

A bridge of this kind lends itself to the measurement of the capacitance of a "leaky" condenser (that is, one having a conducting or current-absorbing dielectric) since it involves a simultaneous balance of resistance, capacitance and inductance. A "leaky" condenser may be treated as a capacitance with a large resistance in parallel or a small resistance in series.⁷ In either case a condition of balance may be obtained by simultaneous adjustment of capacitance and resistance in the proper arms of the bridge. Therefore, determinations of the capacitance may be made as if the resistance were not there. The determination of the dielectric constant may then be accomplished in the usual manner.

The source of alternating current is "D," which in this case is simply a Hartley circuit. A honeycomb coil, "E," is placed in inductive relation to the inductance "F" of the Hartley circuit. A two stage amplifier, "G," made by the General Radio Co., Cambridge, Mass., serves to detect the signals. "R₁" and "R₂" are non-inductive resistance (Curtis) coils of 1000 ohms each. In arm "3" is placed a variable air capacitance "C₁" of 2000 MMF, shunted by a resistance "R₃," variable by steps between 10 and 10,000 ohms. In the fourth arm of the bridge is placed the standard variable condenser, "C₂," in parallel with the dielectric cell, "C_x," and a continuously variable, non-inductive, liquid resistance "R_x." A large unknown resistance, "R₄," is set up by the "leaky" condenser "C_x." The dielectric cell and the standard condenser are the same as employed in the resonance circuit and have been described previously.⁶ Condensers

"C₁," "C₂" and "C_x" are so arranged that the stator plates are attached to the ground "d," thus effecting a shielding the same as in the resonance circuit.

The principle of detection is briefly as follows. Oscillations of a very high frequency are set up in "D." Oscillations of a frequency approaching that of "D" are set up in "G." When the current flows between "a" and "b," audible beats are set up between the two frequencies, which cease when the bridge is balanced. By proper adjustment of the capacitances and inductances of the two circuits, "D" and "G," it is possible to obtain a loud ringing tone in the telephones which yields a sharp,

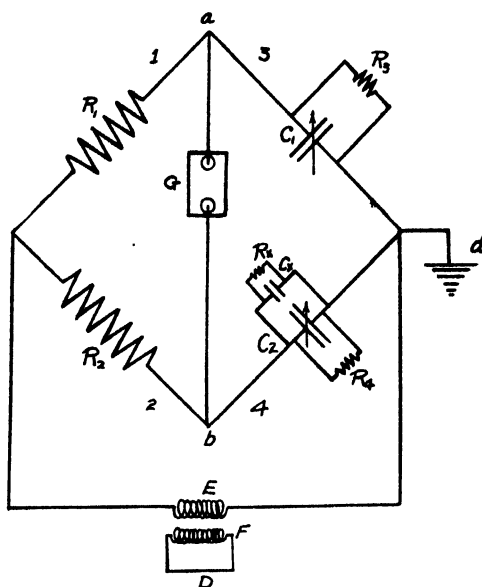


Fig. 1.

R_x—resistance of liquid in condenser C_x; R₁, R₂—1000-ohm Curtis coils; R₃—variable resistance of 10,000-ohms; R₄—variable non-inductive liquid resistance; C₁—variable air condenser of 2000 MMF; C₂—standard variable condenser of 1500 MMF; C_x—dielectric cell; R_x—resistance of liquid in dielectric cell; d—ground.

⁷ Terry, "Advanced Laboratory Practice in Electricity and Magnetism," McGraw-Hill Book Co., New York, 1922, p. 191.

narrow, distinct minimum entirely free from confusion by harmonics. A minimum of width corresponding to 1.5 MMF may be obtained.

Of course this arrangement, employing a very high frequency, is very susceptible to small irregularities in the inductance or capacitance of the bridge arms. By the ordinary methods of balance such an arrangement would be incapable of producing accurate results, since a bridge of this kind is certain to have its balance ratio affected by change of frequency,⁸ and a change of inductance or capacitance in the bridge as is required by the ordinary methods of balance would necessarily alter the frequency greatly. This is true since it is difficult to obtain capacitanceless, inductanceless resistances and leads, and under the usual conditions a so-called "frequency" bridge is almost unavoidable. It is the difficultly controlled stray capacitances and inductances that exist in all ordinary apparatus that cause the trouble. In the apparatus as set up this difficult feature of the very high frequency bridge is avoided by employment of the variable dielectric cell and the continuously variable non-inductive resistance " R_4 ." The measurement is carried out as follows. The bridge is first brought to balance, having " R_3 ," " C_1 ," " C_2 ," " C_x " and " R_4 " all attached as in Fig. 1. The plates of " C_x " are set at a position "A" exactly as in the case of the resonance circuits. The bridge being in balance for this point, " C_x " is adjusted to a point we may again call "B," whereupon " R_x " also changes. The condition of balance is then quite simply restored by adjustment of the standard variable condenser " C_2 " and the non-inductive liquid resistance " R_4 ." Knowing from the resonance method what the capacitance change produced by the change of " C_x " from "A" to "B" in air is, the dielectric constant of a liquid is obtained simply by dividing the change in " C_2 " necessary to restore bridge balance when " C_x " contains that liquid, by this value in air.

The advantage of this method of balance is at once apparent. The arms "1," "2" and "3" are held non-variable for a measurement. Hence for the condition of balance at "B" the relations between the capacitances, resistances and inductances must equal those at "A." Thus we obtain a measurement without change of arm ratios and the fact that we may have a "frequency" bridge presents no difficulties. This method even eliminates the necessity of using Curtis coils at " R_1 " and " R_2 " or of having " R_3 " non-inductive.

The fact that the bridge method described above gives reliable results for the dielectric constants of the mixtures is indicated by a comparison with the results obtained by the electrical resonance method. In a large number of cases it was possible to measure the dielectric constants of the pure liquids and their solutions by both resonance and bridge methods, and in every case a very good agreement was found.

⁸ Ref. 7, p. 186.

The densities of the pure liquids and of the solutions were determined at the same temperature at which their dielectric constants were measured, namely, 25°. An Ostwald-Sprengel pycnometer was used for the purpose. A Pulfrich refractometer was used to measure their refractive indices, also at 25°.

Purification of Materials

Carbon Tetrachloride.—The carbon tetrachloride used was the highest grade material which could be obtained from the Eastman Kodak Company. Since no trace of sulfides was found, it was simply dried and fractionated; b. p. (760 mm.) 76.45–76.52°.

Methyl Acetate.—This material was obtained from the Eastman Kodak Company. It was shaken with a concentrated potassium carbonate solution and washed with water. A rough drying was effected with anhydrous potassium carbonate; then it was completely dehydrated with phosphorus pentoxide. It was fractionated in the usual manner; b. p. (760 mm.) 57.0–57.2°.

Ethyl Acetate.—The ethyl acetate, also obtained from the Eastman Kodak Company, was subjected to a treatment similar to that of the methyl acetate; b. p. (760 mm.) 76.7–76.9°.

Acetone.—The acetone used was an Eastman Kodak Company product. It was crystallized out with sodium iodide and distilled directly from this compound. It was then thoroughly dried (six months) over boric anhydride and fractionated; b. p. (760 mm.) 56.00–56.05°.

Ethyl Alcohol.—A 99% alcohol was purified by the method described by Noyes.⁹

iso-Amyl Alcohol.—This was a Kahlbaum product. After standing over anhydrous copper sulfate for a number of months, it was digested over unslaked lime and fractionated; b. p. (760 mm.) 131.2–131.7°.

The benzene, toluene, chloroform and ethyl ether were purified in the manner described in the preceding papers of this series and their physical constants were essentially the same as those previously reported.

With the exception of the solvent, carbon tetrachloride, all liquids were fractionated immediately before use.

Experimental Results

The experimental work is summarized in Table I. The columns of this table give, from left to right, the mole fraction of the carbon tetrachloride which was used as the solvent, $M.F._{CCl_4}$; the refractive index of the solution, n_D^{25} ; the density of the solution, d_4^{25} ; the observed dielectric constant at 25°, ϵ ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \frac{f_1 m_1 + f_2 m_2}{d} = f_1 P_1 + f_2 P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1 P_1}{f_2}$.

The dielectric constant data for solutions of benzene, toluene, chloroform and ethyl ether in carbon tetrachloride were obtained using the electrical resonance method and are accurate to within one-tenth of one per cent. The dielectric constant data for the other binary mixtures were obtained using the bridge method described above. Wherever possible these

⁹ Noyes, *THIS JOURNAL*, 45, 857 (1923).

tective colloid just before the addition of the ammonium hydroxide, with a view towards stabilizing the lake with the higher concentrations of aluminum. The results for 3 mg. of aluminum are summarized below.

Time in minutes	No starch added	1% starch solution added 5 cc.	10 cc.
10	Coagulated	Suspended	Suspended
20	Settled	Began coagulating	Suspended
180	Signs of coagulation

The effect of starch on the stability of the color intensity was determined using 0.1 mg. of aluminum.

Cc. of 1% starch solution added.....	0.00	0.5	1.0	5.0	10.0
Intensity of color after 25 minutes....	100	106	106	100	82

In the determination of the "sensitiveness" of the test, the experimental method of Horn and Blake^a was used. A series of five solutions was

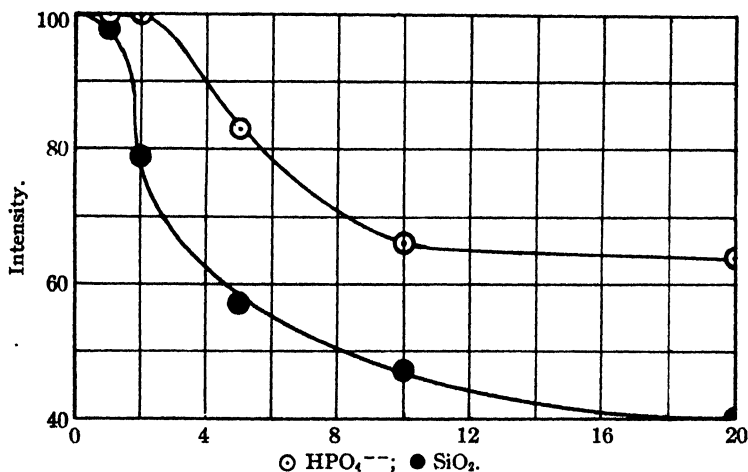


Fig. 6.—Orthophosphate ion and silica.

prepared in marked Nessler tubes of 50cc. capacity, such that the aluminum content of each solution differed from the one immediately before it in the series by a constant amount, the concentration of aluminum in the third solution being that at which the sensitiveness was to be determined. After standing for 25 minutes the tubes were arranged out of their regular order, and four men, separately and unaided, attempted to rearrange them in their proper order. Several such sets of tubes were prepared in which the difference in aluminum content was constant for a given set, though differing from series to series, until finally a series was obtained which could barely be rearranged with certainty by four different persons. The aluminum increment in this series was taken as the amount

^a Horn and Blake, *Am. Chem. J.*, 36, 195 (1906).

of aluminum necessary to produce a difference in the color intensity barely perceptible with certainty at the concentration of the third tube in the series. According to Horn's definition, the reciprocal of this increment in milligrams is the sensitiveness at the given concentration. This procedure was repeated at several concentrations. The results are shown in Table III, in which, according to the nomenclature of Horn, V is the volume in liters of the solution which contains one gram atom of aluminum; B is the milligrams of aluminum in 50 cc. of the solution; Δ is the amount of aluminum in milligrams necessary to produce a perceptible difference in the intensity of 50 cc. of a solution containing B mg. of aluminum; S is the sensitivity and equal to the reciprocal of Δ and $B' = B + \Delta$. The sensitivity curve for aluminum is shown in Fig. 7, in which the square roots of V and S have been employed for convenience in plotting.

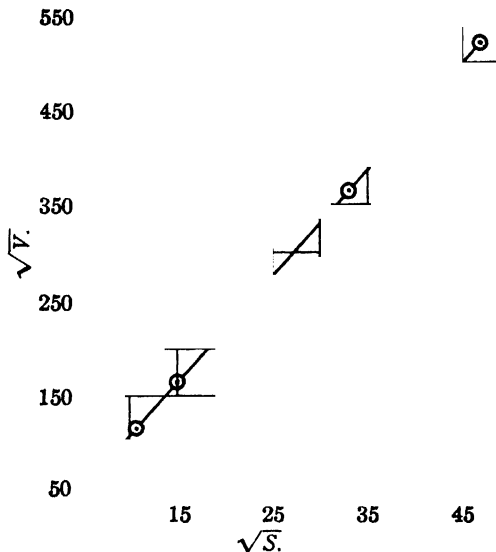


Fig. 7.—Sensitivity curve.

TABLE III
SENSITIVENESS

V	B	Δ	S	B'	Δ/B'	\sqrt{V}	\sqrt{S}
1,355	1.000	Too intense for determination					
2,710	0.500	0.025	40	0.525	0.048	52	6.3
13,550	.100	.009	111	.109	.083	116	10.6
27,000	.050	.0045	222	.0545	.083	165	15.0
135,000	.010	.0009	1111	.0109	.083	365	33.2
271,000	.005	.00045	2220	.00545	.083	520	47.0
1,355,000	.001	Matched solution to which no aluminum had been added					

Determination of Aluminum in Water.—Four samples of water of different iron content were analyzed for aluminum by the three methods described below. The results in parts per million are given in Table IV.

1. The aluminum was determined gravimetrically according to the method given in "Standard Methods of Water Analysis," American Public Health Association, 6th ed., New York, 1925, except that the hydroxides of aluminum and iron were precipitated by adding 5 *N* ammonium hydroxide until the solution was just neutral to methyl red. The iron was determined colorimetrically by the thiocyanate method.

2. A direct determination of the aluminum was made using "Aluminon;" 100–200

cc. of the sample, after the addition of 1-2 cc. of 4 *N* hydrochloric acid, was evaporated to dryness on the water-bath, and the residue ignited at dull redness for a few minutes to destroy any organic matter. After cooling, the ignited residue was taken up with a few drops of 4 *N* hydrochloric acid and 5 cc. of hot water and filtered in order to remove the small amount of silica which had separated. After washing the filter three times with small portions of hot water, the combined filtrate with washings was made neutral to litmus paper by adding 4 *N* hydrochloric acid and transferred to a 50cc. Nessler tube. After the addition of 5 cc. of 1 *N* hydrochloric acid, 5 cc. of 3 *N* ammonium acetate and sufficient distilled water to bring the volume to 30 cc., 5 cc. of 0.1% "Aluminon" solution was added and mixed. When the solution had stood for five minutes, 5 cc. of 5 *N* ammonium hydroxide and 10 cc. of 5 *N* ammonium carbonate were added slowly with constant stirring. The solution was now diluted to 50 cc. and mixed, and after standing for twenty minutes it was compared against standard aluminum solutions in Nessler tubes which were prepared and "aged" in a similar manner. In order to correct for the iron, a quantity of iron equivalent to that found in (1) was added to the standard.

3. In this case the aluminum was separated from the iron. A 300-550cc. sample of the water was treated as stated in (1) above until the precipitates of aluminum and iron hydroxides were filtered the first time. This precipitate was dissolved in 5 cc. of warm 5 *N* nitric acid by pouring the acid through the filter three times, and finally washing the filter three times with small quantities of hot water. The combined filtrate with washings was evaporated on the hot-plate to 1 cc., made strongly alkaline with 6 *N* sodium hydroxide, brought to boiling and filtered through a very small filter paper. The filter was washed three times with small quantities of hot water, and the filtrate with washings, after being made neutral to litmus paper by the addition of hydrochloric acid, was transferred to Nessler tubes and cooled. The procedure was completed from this point in (2) above.

TABLE IV
DETERMINATION OF ALUMINUM IN WATER

Sample	Iron (p.p.m.)	Aluminum (p.p.m.)		
		Method 1, gravimetric	Method 2, direct detn.	Method 3, separation of Fe
I	0.00	0.05	0.05	0.05
II	.66	1.03	.22	1.09
III	.23	0.51	.10	0.41
IV	5.00	.59	.12	.62

Discussion

The results for "aging" with 2 cc. of ammonium hydroxide, where the solutions were "aged" in the light and dark, respectively, are represented graphically in Fig. 1. There is little difference at any time between the intensities in the two cases. Although the curves diverge from each other in the manner which is to be expected if light has an appreciable effect on the stability of the color, the maximum difference of about 2% is within the limits of the experimental error. Thus, the rate of decrease in intensity appears to be independent of the diffused light of the laboratory.

The lower curves in Fig. 1 show the effect of the concentration of the ammonium hydroxide. Here, as in each case studied, the period of "aging" may be divided into two parts according to whether the slope

of the curve is "steep" or "flat." With the addition of ammonium hydroxide a comparatively short interval begins, in which the rate of decrease in intensity is very rapid. This period merges into the second and comparatively long period of slow change in intensity. With 2 cc. of ammonium hydroxide the first stage is 35 minutes long, while with 5 cc. this time is almost halved; however, in the latter instance the intensity is decreased by about 15% in the second period.

In Figs. 2 and 3 are shown the effects of varying the quantities of the reagents. The intensity increases with the concentration of hydrochloric acid to a maximum value, then drops rapidly on a further increase in the acid concentration. With an increase in the quantity of ammonium hydroxide, the intensity decreases along a curve which is very similar to the curves for "aging." The effect of ammonium carbonate is least of all, being a decrease in intensity of about 15% for 13 cc. of the reagent. In the case of the other three reagents the intensity increases with the concentration.

For the colorimetric determination of aluminum with "Aluminon" a procedure has been given which is in accord with the facts brought out in the foregoing curves. The quantities of the reagents, the time given for lake formation and all other conditions have been chosen, where possible, so that slight variations in the several factors will produce a minimum effect on the final color intensity and, therefore, a minimum error in the determination. Since the test is fairly sensitive to a change in the acid concentration, the solution to be examined for aluminum must be neutral at the time the hydrochloric acid is added. Furthermore, since the curves for the change in intensity with temperature and the time at lake formation are quite steep, it is obvious that the unknown solution and the standards must be at the same temperature during lake formation, and that the time intervals must also be of equal length. Where the analyst has the time, something in accuracy may be gained by giving a longer period for the lake to form.

Certain substances interfere with the test, and in this connection the effect of several ions likely to be encountered in water analysis has been studied. One mg. of silica or 2 mg. of HPO_4^{--} may be present without the results being impaired. While the orthophosphate ion tends to give low results by preventing the formation of the aluminum lake, the normal phosphate ion causes a turbidity which tends towards high results. Similarly, calcium and manganese produce turbid solutions. Some numerical values for the permissible quantities per 50 cc. of solution are given in Table II.

The results in Table I seem to indicate that iron may be present with aluminum in the ratio of 1:10 without vitiating the results. However, if as much as a few hundredths of a milligram of iron is present, a separa-

tion is necessary regardless of the ratio, since the combined iron and aluminum lakes will give a solution which is too deeply colored for accurate comparison. A fairly rapid procedure for the separation of iron from aluminum has been described with which results have been obtained by the "Aluminon" method for several samples of water that agree closely with the values for the aluminum content found by the longer and more tedious gravimetric method.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

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Since the bridge as set up contains several novel features it will be briefly described. It is shown diagrammatically in Fig. 1. The instantaneous potential of an alternating current for any given instant is determined by the "phase angle" obtained in a vectorial consideration of the inductance and capacitance. The phase angle of the current at the point "a" must equal the phase angle of the current at "b" in order that the points "a" and "b" be at equal potential at all times and that no current be detectable in "G." Since the phase angle is dependent on the resistance, inductance and capacitance in the arms, then in this sort of bridge a balance of resistance and inductance is required along with a balance of capacitance.

¹ Williams and Krchma, *THIS JOURNAL*, 49, 1676 (1927).

² Lange, *Z. Physik*, 33, 169 (1925).

³ Debye, "Handbuch der Radiologie" (Marx), 6, 625 (1925).

⁴ Smyth, *THIS JOURNAL*, 49, 1030 (1927).

⁵ Debye, *Phys. Z.*, 13, 97 (1912); *Verhandl. deut. phys. Ges.*, 15, 777 (1913).

⁶ Williams and Krchma, *THIS JOURNAL*, 48, 1888 (1926).

A bridge of this kind lends itself to the measurement of the capacitance of a "leaky" condenser (that is, one having a conducting or current-absorbing dielectric) since it involves a simultaneous balance of resistance, capacitance and inductance. A "leaky" condenser may be treated as a capacitance with a large resistance in parallel or a small resistance in series.⁷ In either case a condition of balance may be obtained by simultaneous adjustment of capacitance and resistance in the proper arms of the bridge. Therefore, determinations of the capacitance may be made as if the resistance were not there. The determination of the dielectric constant may then be accomplished in the usual manner.

The source of alternating current is "D," which in this case is simply a Hartley circuit. A honeycomb coil, "E," is placed in inductive relation to the inductance "F" of the Hartley circuit. A two stage amplifier, "G," made by the General Radio Co., Cambridge, Mass., serves to detect the signals. "R₁" and "R₂" are non-inductive resistance (Curtis) coils of 1000 ohms each. In arm "3" is placed a variable air capacitance "C₁" of 2000 MMF, shunted by a resistance "R₃," variable by steps between 10 and 10,000 ohms. In the fourth arm of the bridge is placed the standard variable condenser, "C₂," in parallel with the dielectric cell, "C_x," and a continuously variable, non-inductive, liquid resistance "R_x." A large unknown resistance, "R₄," is set up by the "leaky" condenser "C_x." The dielectric cell and the standard condenser are the same as employed in the resonance circuit and have been described previously.⁶ Condensers

"C₁," "C₂" and "C_x" are so arranged that the stator plates are attached to the ground "d," thus effecting a shielding the same as in the resonance circuit.

The principle of detection is briefly as follows. Oscillations of a very high frequency are set up in "D." Oscillations of a frequency approaching that of "D" are set up in "G." When the current flows between "a" and "b," audible beats are set up between the two frequencies, which cease when the bridge is balanced. By proper adjustment of the capacitances and inductances of the two circuits, "D" and "G," it is possible to obtain a loud ringing tone in the telephones which yields a sharp,

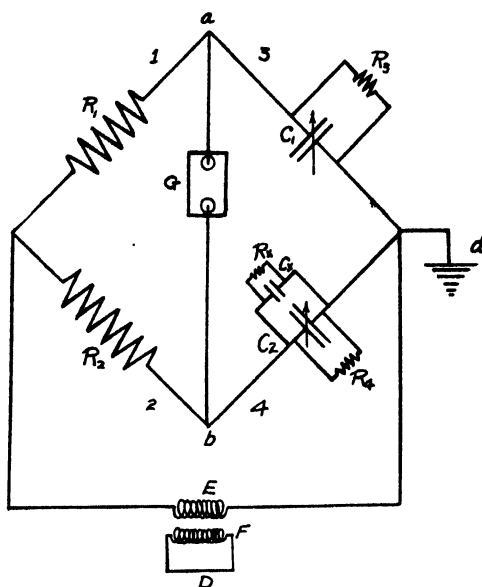


Fig. 1.

R_x—resistance of liquid in condenser C_x; R₁, R₂—1000-ohm Curtis coils; R₃—variable resistance of 10,000-ohms; R₄—variable non-inductive liquid resistance; C₁—variable air condenser of 2000 MMF; C₂—standard variable condenser of 1500 MMF; C_x—dielectric cell; R_x—resistance of liquid in dielectric cell; d—ground.

⁷ Terry, "Advanced Laboratory Practice in Electricity and Magnetism," McGraw-Hill Book Co., New York, 1922, p. 191.

narrow, distinct minimum entirely free from confusion by harmonics. A minimum of width corresponding to 1.5 MMF may be obtained.

Of course this arrangement, employing a very high frequency, is very susceptible to small irregularities in the inductance or capacitance of the bridge arms. By the ordinary methods of balance such an arrangement would be incapable of producing accurate results, since a bridge of this kind is certain to have its balance ratio affected by change of frequency,⁸ and a change of inductance or capacitance in the bridge as is required by the ordinary methods of balance would necessarily alter the frequency greatly. This is true since it is difficult to obtain capacitanceless, inductanceless resistances and leads, and under the usual conditions a so-called "frequency" bridge is almost unavoidable. It is the difficultly controlled stray capacitances and inductances that exist in all ordinary apparatus that cause the trouble. In the apparatus as set up this difficult feature of the very high frequency bridge is avoided by employment of the variable dielectric cell and the continuously variable non-inductive resistance " R_4 ." The measurement is carried out as follows. The bridge is first brought to balance, having " R_3 ," " C_1 ," " C_2 ," " C_x " and " R_4 " all attached as in Fig. 1. The plates of " C_x " are set at a position "A" exactly as in the case of the resonance circuits. The bridge being in balance for this point, " C_x " is adjusted to a point we may again call "B," whereupon " R_x " also changes. The condition of balance is then quite simply restored by adjustment of the standard variable condenser " C_2 " and the non-inductive liquid resistance " R_4 ." Knowing from the resonance method what the capacitance change produced by the change of " C_x " from "A" to "B" in air is, the dielectric constant of a liquid is obtained simply by dividing the change in " C_2 " necessary to restore bridge balance when " C_x " contains that liquid, by this value in air.

The advantage of this method of balance is at once apparent. The arms "1," "2" and "3" are held non-variable for a measurement. Hence for the condition of balance at "B" the relations between the capacitances, resistances and inductances must equal those at "A." Thus we obtain a measurement without change of arm ratios and the fact that we may have a "frequency" bridge presents no difficulties. This method even eliminates the necessity of using Curtis coils at " R_1 " and " R_2 " or of having " R_3 " non-inductive.

The fact that the bridge method described above gives reliable results for the dielectric constants of the mixtures is indicated by a comparison with the results obtained by the electrical resonance method. In a large number of cases it was possible to measure the dielectric constants of the pure liquids and their solutions by both resonance and bridge methods, and in every case a very good agreement was found.

⁸ Ref. 7, p. 186.

The densities of the pure liquids and of the solutions were determined at the same temperature at which their dielectric constants were measured, namely, 25°. An Ostwald-Sprengel pycnometer was used for the purpose. A Pulfrich refractometer was used to measure their refractive indices, also at 25°.

Purification of Materials

Carbon Tetrachloride.—The carbon tetrachloride used was the highest grade material which could be obtained from the Eastman Kodak Company. Since no trace of sulfides was found, it was simply dried and fractionated; b. p. (760 mm.) 76.45–76.52°.

Methyl Acetate.—This material was obtained from the Eastman Kodak Company. It was shaken with a concentrated potassium carbonate solution and washed with water. A rough drying was effected with anhydrous potassium carbonate; then it was completely dehydrated with phosphorus pentoxide. It was fractionated in the usual manner; b. p. (760 mm.) 57.0–57.2°.

Ethyl Acetate.—The ethyl acetate, also obtained from the Eastman Kodak Company, was subjected to a treatment similar to that of the methyl acetate; b. p. (760 mm.) 76.7–76.9°.

Acetone.—The acetone used was an Eastman Kodak Company product. It was crystallized out with sodium iodide and distilled directly from this compound. It was then thoroughly dried (six months) over boric anhydride and fractionated; b. p. (760 mm.) 56.00–56.05°.

Ethyl Alcohol.—A 99% alcohol was purified by the method described by Noyes.⁹

iso-Amyl Alcohol.—This was a Kahlbaum product. After standing over anhydrous copper sulfate for a number of months, it was digested over unslaked lime and fractionated; b. p. (760 mm.) 131.2–131.7°.

The benzene, toluene, chloroform and ethyl ether were purified in the manner described in the preceding papers of this series and their physical constants were essentially the same as those previously reported.

With the exception of the solvent, carbon tetrachloride, all liquids were fractionated immediately before use.

Experimental Results

The experimental work is summarized in Table I. The columns of this table give, from left to right, the mole fraction of the carbon tetrachloride which was used as the solvent, $M.F._{CCl_4}$; the refractive index of the solution, n_D^{25} ; the density of the solution, d_4^{25} ; the observed dielectric constant at 25°, ϵ ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \frac{f_1 m_1 + f_2 m_2}{d} = f_1 P_1 + f_2 P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1 P_1}{f_2}$.

The dielectric constant data for solutions of benzene, toluene, chloroform and ethyl ether in carbon tetrachloride were obtained using the electrical resonance method and are accurate to within one-tenth of one per cent. The dielectric constant data for the other binary mixtures were obtained using the bridge method described above. Wherever possible these

⁹ Noyes, *THIS JOURNAL*, 45, 857 (1923).

values were checked using the more accurate resonance method. This was always possible in the case of the solutions containing the highest mole fractions of the solvent. It may be pointed out here that these are the

TABLE I
DIELECTRIC CONSTANT AND DENSITY DATA

1. Carbon Tetrachloride-Benzene ^a					
M F CCl ₄	n_D^{25}	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.00	1.45724	1.5835	2.230	28.24	26.73
0.75	1.46747	1.4159	2.240	27.85	26.73
.50	1.47766	1.2433	2.253	27.46	26.73
.25	1.48770	1.0624	2.267	27.09	26.73
.10	1.49738	0.9498	2.274	26.83	26.73
.0	1.49780	.8731	2.282	26.73	26.73
2. Carbon Tetrachloride-Toluene					
1.00	1.45724	1.5835	2.230	28.23	33.66
0.90	...	1.5053	2.246	28.78	33.66
.75	1.46798	1.3880	2.271	29.62	33.66
.50	1.47605	1.2048	2.310	31.02	33.66
.0	1.49392	0.8593	2.378	33.66	33.66
3. Carbon Tetrachloride-Chloroform					
1.00	1.45724	1.5835	2.230	28.23	49.8
0.75	1.45433	1.5602	2.682	33.43	49.0
.50	1.45062	1.5350	3.215	37.80	47.4
.25	1.44720	1.5082	3.901	41.70	46.2
.0	1.44394	1.4978	4.770	44.93	44.9
4. Carbon Tetrachloride-Ethyl Ether					
1.00	1.45724	1.5835	2.230	28.23	56.0
0.75	1.43127	1.3583	2.722	35.75	58.2
.50	1.40448	1.1375	3.210	42.48	56.7
.35	1.38843	...	3.491	46.09	55.7
.25	1.37782	0.9197	3.700	48.39	55.1
.0	1.34993	.7079	4.265	54.54	54.5
5. Carbon Tetrachloride-Methyl Acetate					
1.00	1.45724	1.5835	2.230	28.23	78.0
0.90	1.44976	1.5256	2.610	33.32	79.0
.75	1.43458	1.4400	3.192	39.20	72.1
.50	1.41133	1.2840	4.225	45.96	63.7
.362	1.39795	...	4.880	48.63	60.4
.25	1.38593	1.1134	5.400	50.13	57.4
.0	1.35938	0.9272	6.680	52.26	52.3
6. Carbon Tetrachloride-Ethyl Acetate					
1.00	1.45724	1.5835	2.230	28.23	87.0
0.75	1.43519	1.4101	3.220	41.42	81.0
.50	1.41312	1.2530	4.201	50.47	72.7
.25	1.39134	1.0657	5.11	56.64	66.1
.0	1.36948	0.8946	6.03	61.65	61.6

TABLE I (Concluded)
 7. Carbon Tetrachloride-Acetone

M.F. CCl_4	n_D^{20}	d_4^{20}	ϵ	$P_{1,2}$	P_1
1.00	1.45724	1.5835	2.230	28.23	170.0
0.90	1.45036	1.5215	3.28	40.93	155.1
.75	1.43780	1.4260	4.98	51.98	123.2
.70	1.43378	1.3906	5.67	54.72	116.5
.60	1.42494	1.3202	6.17 ^b	66.06	122.8
.0	1.35695	0.7855	21.3	64.38	64.4

8. Carbon Tetrachloride-Ethyl Alcohol

1.00	1.45724	1.5835	2.230	28.23	73.5
0.90	1.45106	1.5325	2.560	31.91	64.9
.75	1.44082	1.4491	3.74	41.88	82.8
.60	1.42926	1.3540	5.45	48.83	79.7
.50	1.42042	1.2833	7.05	51.72	75.2
.0	1.35894	0.7862	25.2	52.13	52.1

9. Carbon Tetrachloride-*iso*-Amyl Alcohol

1.00	1.45724	1.5835	2.230	28.23	86.0
0.90	1.45106	1.4965	2.502	32.81	74.0
.75	1.44273	1.3700	3.127	41.54	81.4
.60	1.43468	1.2453	4.61 ^b	55.89	97.4
.0	1.40568	0.8083	14.55	89.24	89.2

* Data previously reported.

^b Values do not fall on smooth curve.

most important points of the whole curve, since it is the electric moment of a single solute molecule completely surrounded by the electrically inert solvent molecules that is desired. The value of the molar polarization of the second component is obtained by taking a tangent to the $P_{1,2}$ -mole fraction curve at the point where the mole fraction of the reference liquid is unity and prolonging it to cut the axis where the mole fraction of the solute is unity. The dielectric constant data obtained for these binary mixtures are accurate to within three-tenths of one per cent.

Discussion of Results

The results obtained from the dielectric constant and density data using carbon tetrachloride as a non-polar solvent for certain organic molecules are in all respects similar to those obtained from the binary liquid mixtures considered in the preceding paper¹ in which benzene was used as the solvent. As before, the assumption is made that the polarization due to the non-polar solvent, carbon tetrachloride, is always directly proportional to its mole fraction in solution. The results obtained for the various binary mixtures reported in this article seem to indicate the correctness of this assumption.

It is convenient to divide the systems studied into two groups. For a detailed discussion of this method of grouping of the systems the reader is referred to the article in which the benzene systems are reported.¹

GROUP 1.—Those in which the molar polarization of the second component, P_2 , is constant throughout the whole range of concentration.

1. Carbon Tetrachloride-Benzene
2. Carbon Tetrachloride-Toluene

GROUP 2.—Those in which P_2 is not a constant.

3. Carbon Tetrachloride-Chloroform
4. Carbon Tetrachloride-Ethyl Ether
5. Carbon Tetrachloride-Methyl Acetate
6. Carbon Tetrachloride-Ethyl Acetate
7. Carbon Tetrachloride-Acetone
8. Carbon Tetrachloride-Ethyl Alcohol
9. Carbon Tetrachloride-*iso*-Amyl Alcohol

Calculation of the Electric Moments of the Molecules

The electric moments of the solute molecules have been calculated from the values of their molar polarizations, P_2 . This molar polarization contains two terms, a polarization due to an orientation effect, P'_2 , and a polarization due to a deformation effect, P''_2 . Since the polarization due to the deformation of the molecule may be approximated by the familiar Lorenz-Lorentz formula,^{1,2,3,10} the polarization due to the orientation effect may be calculated. This term contains the electric moment of the molecule, μ , in the following manner, $P'_2 = \frac{4\pi}{3} N \frac{\mu^2}{3kT}$, where the symbols have their usual significance.¹

The electric moments of the several solute molecules, calculated from dielectric constant and density of their solutions in carbon tetrachloride, are given in Table II.

TABLE II
ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P''_2 , cc.	P'_2 cc.	$\mu \times 10^{18}$
Benzene	25.8	0.9	0.06
Toluene	30.3	3.4	.40
Chloroform	21.3	28.5	1.15
Ethyl ether	23.0	33.0	1.24
Methyl acetate	18.0	60.0	1.67
Ethyl acetate	22.2	64.8	1.74
Acetone	16.0	154.0	2.70
Ethyl alcohol	16.0	57.5	1.63
<i>iso</i> -Amyl alcohol	13.0	73.0	1.85

Discussion of Table of Electric Moments

The value of the electric moment of benzene is of considerable interest. Smyth,¹¹ using various physical constants, calculated its moment to be

¹⁰ Lorentz, *Wied. Ann.*, 9, 641 (1880).

¹¹ Smyth, *THIS JOURNAL*, 46, 2151 (1924).

0.2×10^{-18} , a value so small as to be indistinguishable from zero by the method of calculation employed and recognized by Smyth as indicating that the molecule of benzene had little, if any, moment. Sanger¹² concluded from a careful consideration of the accurate measurements of the dielectric constant of liquid benzene by Graffunder¹³ that the moment of the benzene molecule must be practically zero. The value presented above for benzene in the liquid state indicates that if benzene has any moment at all it must be of an exceedingly small magnitude and must, therefore, be considered as experimental verification of the calculations and conclusions of Smyth and Sanger.

The toluene molecule is found to have a moment $\mu = 0.40 \times 10^{-18}$. This value is, without doubt, more reliable than the value (0.52×10^{-18}) reported in the previous paper.¹ It was stated in that article that the latter value was somewhat larger than might have been predicted, and the reasons were given.

Chloroform and ethyl ether are found to have moments which are almost identical in value with those calculated from the dielectric constant and density data of their solutions in benzene, which, in turn, were shown to be in excellent agreement with values found by other investigators.^{1,2,14}

The values obtained for the methyl acetate and ethyl acetate molecules are not widely different in magnitude. There can be no doubt from the results of the experimental work that the moment of the ethyl acetate molecule, in carbon tetrachloride solution at least, is the larger of the two. This tends to confirm the statement of Smyth¹¹ that organic molecules having longer carbon chains will have higher electric moments. His statements are again confirmed by the calculations reported above for the ethyl alcohol and *iso*-amyl alcohol molecules. Their moments are of the expected order of magnitude. Miss Lange² determined the moments of a number of the three, four and five carbon alcohols in benzene solution, finding values between 1.53 and 1.83×10^{-18} . *Iso*-amyl alcohol was assigned the value 1.76×10^{-18} . The value for the moment of ethyl alcohol was not reported by this investigator. Her values show this tendency to increase as the length of the carbon chain is increased.

Acetone gives the largest moment of any molecule reported in this paper. It is a fact that the measurements of the dielectric constants for the system carbon tetrachloride-acetone were the most difficult of any of the systems herein reported, yet satisfactory check determinations were obtained for the concentrations studied. The greatest uncertainty lies in the extrapolation of the tangent to the $P_{1,2}$ -mole fraction carbon tetrachloride curve to obtain the molar polarization, P_2 , of a single acetone molecule completely

¹² Sanger, *Physik. Z.*, 27, 165 (1926).

¹³ Graffunder, *Ann. Physik.*, 70, 225 (1923).

¹⁴ Sanger, *Physik. Z.*, 27, 556 (1926)

surrounded by carbon tetrachloride molecules. A slight movement of the position of the tangent makes considerable difference in the P_2 value obtained. Extreme care has been taken to obtain an accurate tangent, and it is believed that the value reported for the moment of the acetone molecule is significant. It is in excellent agreement with the value, $\mu = 2.61 \times 10^{-18}$, reported by Loeb¹⁸ in his recent book.

Summary

1. Dielectric constant and density data at 25° for eight binary liquid mixtures have been determined at various concentrations. The systems studied were solutions of toluene, chloroform, ethyl ether, methyl acetate, ethyl acetate, acetone, ethyl alcohol and *iso*-amyl alcohol dissolved in carbon tetrachloride.

2. The various systems have been grouped according to whether or not the molar polarization of the solute in solution changes with concentration.

3. The electric moments of each of the solute molecules in carbon tetrachloride solution have been calculated using the Langevin-Debye modification of the Clausius-Mossotti Law. These results have been critically discussed. Wherever possible they have been compared with the results obtained by other investigators.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. IV BENZENE AS A SOLVENT FOR CERTAIN SOLID SUBSTANCES

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The previous papers of this series^{1,2,3} have dealt with the dielectric constants of binary liquid mixtures of particular types. The systems to be discussed in this article consist of a solvent, benzene, and certain solid solutes, substances which, with one exception, have been described in the literature as being relatively non-polar in character. The solubility relations of these systems as well as of a number of other similar systems have been the subject of considerable study, the chief results of which are given by Hildebrand.⁴ This author points out that they are governed by certain regularities, particularly as regards their relative internal pressures; and yet numerous exceptions to these generalizations

¹⁸ Loeb, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, 1927, p. 408.

¹ Williams and Krchma, *THIS JOURNAL*, **48**, 1888 (1926).

² Williams and Krchma, *ibid.*, **49**, 1676 (1927).

³ Krchma and Williams, *ibid.*, **49**, 2408 (1927).

⁴ Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, Chapter 14.

are known and have been the subject of much speculation. The terms "polar" and "non-polar" are continually used in such discussions, terms which can be but qualitative in nature. The present authors believe that if sufficient dielectric constant data were available for solutions of the type referred to above, the polarities of the molecules involved might be quantitatively expressed and certain explanations given to account for irregular solubility relations, for certain it is that the dielectric constant gives the most direct evidence that is available concerning polarity. The accumulation of these data will, of course, require a number of years and the results on the benzene systems to be given in this paper can only be considered as a beginning. The work is being continued in this Laboratory.

For the present it is of sufficient interest to calculate the electric moments of the various solute molecules in the electrically inert solvent, benzene. These moments are to be calculated from dielectric constant and density data, using the Langevin⁵-Debye⁶ concept of molar polarizability. The equations actually used have been presented in the second paper of this series.² In all cases the symbols used in that paper have been retained.

Method

The method used for the determination of the dielectric constant of the benzene and of its solutions was the electrical resonance method described in the first paper of the series,¹ using the same frequency, 10^6 cycles per second. The measurements were made at 25°.

Density determinations on the solutions were made. In all cases a fifty cc. pycnometer of the Ostwald-Sprengel type was used.

Purification of Materials

Benzene.—The benzene, obtained from the Eastman Kodak Company, was treated in the usual manner to remove thiophene, after which it gave no test for this substance. It was purified by fractional crystallizations and distillations until the liquid gave practically the same physical constants as are given by Richards and Shipley.⁷ The fraction used boiled between 80.15 and 80.22°, corrected to 760 mm. pressure, and had a density, d_{25}^{25} , 0.8748.

Benzoic Acid (C_6H_5COOH).—This material, obtained from the Mallinckrodt Chemical Company, was recrystallized from toluene and sublimed. The final product was in the form of pure, white crystals having a melting point of 121.8°.

Phenol (C_6H_5OH).—This substance, obtained from Merck and Company under the label "U. S. P.—C. P.—Loose Crystals" was melted and fractionally distilled. The fraction used boiled between 179.5 and 180.0°.

Iodine (I_2).—The iodine, a Mallinckrodt product, was simply resublimed and used without further treatment.

Antimony Iodide (SbI_3).—This material was obtained through the kindness of

⁵ Langevin, *Ann. chim. phys.*, 5 [8], 70 (1905).

⁶ Debye, *Physik. Z.*, 13, 97 (1912); "Handbuch der Radiologie" (Marx), 6, 597 (1925).

⁷ Richards and Shipley, *THIS JOURNAL*, 41, 2022 (1919).

Mr. R. W. Gooding of this University. It had been subjected to a very careful purification by repeated recrystallizations from carbon tetrachloride.

Stannic Iodide (SnI_4).—The stannic iodide was a Kahlbaum product which had been carefully preserved in a pure condition. It was presented by Professor J. H. Walton of this department.

Silver Perchlorate (AgClO_4).—This salt was prepared by the G. Frederick Smith Manufacturing Company of Urbana, Illinois. Dr. Smith⁸ did not give details of the method used except to say that it was dehydrated in vacuo at 135° for thirty hours and at ordinary pressure for sixty hours at the same temperature. It gave no test for perchloric acid.

Experimental Results

The experimental data are presented in Table I. The columns of this table give, from left to right: the per cent. by weight of benzene which was used as solvent, %, C_6H_6 ; the mole fraction of benzene, M. F., C_6H_6 ; the density of the solution, d_{25}^{25} ; the observed dielectric constant of the solution, ϵ ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 m_1 + f_2 m_2}{d}$ = $f_1 P_1 + f_2 P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1 P_1}{f_2}$.

TABLE I
DIELECTRIC CONSTANT AND DENSITY DATA AT 25°

1. Benzene-Benzic Acid

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	43.5
99.25	.995	.8763	2.287	26.77	43.5
98.50	.990	.8780	2.290	26.86	43.5
97.78	.986	.8796	2.294	27.01	43.5
97.06	.981	.8812	2.309	27.20	43.5
96.35	.976	.8828	2.314	27.32	43.5
95.65	.972	.8842	2.322	27.41	43.5
94.28	.963	.8874	2.332	27.57	43.5
92.96	.954	.8904	2.340	27.74	43.5
92.00	.947	.8923	2.371	28.23	43.5

2. Benzene-Phenol

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	89.0
96.12	.968	.8813	2.403	28.44	89.0
91.67	.930	.8887	2.567	30.54	89.0
87.90	.897	.8929	2.765	32.76	89.0
84.61	.869	.9015	2.913	34.64	89.0
77.73	.808	.9153	3.300	38.48	89.0
73.34	.768	.9243	3.602	41.01	89.0
61.12	.655	.9461	4.664	48.47	89.0

⁸ The authors wish to take this opportunity to thank Dr. Smith for his extreme generosity in furnishing this material for the work.

TABLE I (Concluded)

3. Benzene-Iodine

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.000	0.8748	2.280	26.68	60.2
99.10	.998	.8817	2.285	26.75	60.2
98.20	.994	.8861	2.295	26.90	60.2
96.77	.990	.8984	2.310	27.05	60.2
96.49	.989	.9000	2.316	27.09	60.2
93.75	.979	.9211	2.335	27.31	60.2

4. Benzene-Antimony Tri-iodide

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.282	26.68	
99.86	.9998	.8758	2.285	26.74	
99.83	.9997	.8763	2.287	26.77	
99.67	.9995	.8773	2.291	26.88	
99.50	.9992	.8788	2.300	26.95	

5. Benzene-Stannic Iodide

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.280	26.68	26.7
99.83	.9998	.8754	2.282	26.68	26.7
99.67	.9996	.8770	2.284	26.69	26.7
99.17	.9990	.8801	2.288	26.68	26.7
99.01	.9988	.8813	2.290	26.68	26.7
98.68	.9983	.8838	2.291	26.65	26.7
97.84	.9973	.8888	2.297	26.59	26.7

6. Benzene-Silver Perchlorate

%, C_6H_6	M.F., C_6H_6	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
100.00	1.0000	0.8748	2.280	26.68	477.0
99.66	.9987	.8770	2.336	27.44	477.0
99.27	.9973	.8790	2.384	28.12	477.0
98.58	.9946	.8832	2.454	29.13	477.0
97.64	.9909	.8940	2.597	30.85	477.0

It will be observed that these data differ from those of the previous articles^{2,3} in that it was not possible to determine the densities and dielectric constants of the solutions over a wide range of concentration. In the case of the binary liquid mixtures the two components were mutually soluble in all proportions. In the case of the solid substances used as solutes in Table I it was possible to make the measurements over but a small range of concentration, due to their limited solubility. However, with one exception (antimony tri-iodide) it was possible to dissolve enough of the solute in benzene so that when the molar polarization of the solution, $P_{1,2}$, was plotted against mole fraction of the solvent, a curve was obtained from which a significant value for the molar polarization of the second component or the solute, P_2 , resulted. It was found for each of the five

solutes reported that its molar polarization in solution was exactly proportional to its mole fraction in solution over the range of its solubility. Thus, taking the tangent to the $P_{1,2}$ curve at the point where the mole fraction of the solvent is unity and prolonging it to cut the axis where the mole fraction of the other component would be unity consisted simply of a mathematical extrapolation.

Calculation of the Electric Moments of the Molecules

The electric moments of the various solute molecules have been calculated from their molar polarizations after the manner described in the second article of this series,² using the equation $P_2 = P'_2 + P''_2$, where P'_2 = polarization due to orientation of molecule = $\frac{4\pi}{3} N \frac{\mu^2}{kT}$; and P''_2 = polarization due to deformation of molecule = $\frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{M}{d}$.

The term P''_2 has been approximated in each case using data obtained either from the Landolt-Börnstein "Tabellen" or from Volume I of the "International Critical Tables." If these values are in error by 5 cc., an improbable value, the electric moments as reported are not changed by a correction of this magnitude since they have been reported to two significant figures only.

The electric moments of solute molecules, computed as indicated above, are presented in Table II.

TABLE II
ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2	P'_2	P''_2	$\mu \times 10^{18}$
C_6H_5COOH	43.5	24.6	19	1.0
C_6H_5OH	89.0	27.7	61	1.7
I_2	60.2	20	40	1.4
SnI_4	26.7	30	...	0.0
$AgClO_4$	477.0	16	461	4.7

Discussion of Table of Electric Moments

C_6H_5COOH .—It has been shown by Nernst⁹ from distribution experiments that benzoic acid in benzene solution undergoes a polymerization which may be represented by means of the equation $2C_6H_5COOH \rightarrow (C_6H_5COOH)_2$. It is difficult at present to state exactly what the effect of this association is upon the value of the electric moment reported in the above table. Values for the electric moments of water and ammonia in liquid or associated condition, and in vapor or non-associated condition, reported by Smyth¹⁰ indicate that the effect of association is to lower the electric moment.

⁹ Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

¹⁰ Smyth, *THIS JOURNAL*, **46**, 2151 (1924).

C₂H₅OH.—The value of the moment of this molecule was reported in a preceding paper of this series.² It is in excellent agreement with the value calculated by Smyth¹¹ from the experimental data of Philip and Haynes,¹² and will not be discussed further here.

I₂.—The magnitude of the moment found for the iodine molecule was higher than might have been expected, since that molecule has been considered as a symmetrical one. A symmetrical molecule should, of course, give no moment, a fact which has actually been shown experimentally for gases like hydrogen and nitrogen.¹³ However, Lewis¹⁴ has explained that a symmetrical molecule like iodine may become polarized in one direction or another. This polarization means that the molecule will have an electric moment. Lewis shows that this polarization extends to a slight ionization in the case of iodine, and that bromine, chlorine, fluorine and hydrogen, in the order named, show a diminishing tendency toward this ionization. Table III, presented below, shows that this is also the order of decreasing electric moments or, what is equivalent, the order of decreasing polarity.

TABLE III

COMPARISON OF MOMENTS OF HALIDE MOLECULES AND HYDROGEN

Molecule.....	Iodine	Bromine	Chlorine	Fluorine	Hydrogen
$\mu \times 10^{18}$	1.4	0.58 ¹⁵	0.13 ¹⁶	0.0 ¹³

In making the calculation for the electric moment of the iodine molecule the chemical changes taking place upon its solution have not been considered. These chemical changes have been discussed at length by Hildebrand.¹⁷ The present authors are of the opinion that these changes in the dilute iodine solutions did not materially affect the accuracy of the calculation, the result of which is reported above. In the method used for the calculation of the moment it is necessary to assume that the polarization due to the solvent, in this case benzene, is always directly proportional to its mole fraction in solution. This assumption, as has already been indicated,² may lead to somewhat erroneous conclusions since it does not take into account what has been termed the chemistry of solution. However, the solution of iodine in benzene has been found to be ideal with respect to its molar polarization in solution over the range

¹¹ Smyth, *THIS JOURNAL*, **49**, 1030 (1927).

¹² Philip and Haynes, *J. Chem. Soc.*, **87**, 998 (1905).

¹³ Von Braunmühl, *Physik. Z.*, Forthcoming Publication.

¹⁴ Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, 1923, p. 83.

¹⁵ Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909).

¹⁶ Eversheim, *Ann. Physik*, [4] **13**, 492 (1904). The values of the moments of chlorine and bromine were calculated by Smyth from these data.

¹⁷ Hildebrand, *ref. 4*, pp. 148-151.

of concentration studied, since when this molar polarization is plotted against the mole fraction of the solvent a straight line results. This fact seems to eliminate the possibility of chemical interference.

SnI₄.—That the stannic iodide molecule would show a zero moment might have been predicted from atomic structure considerations. It has always been considered as a "non-polar" substance by Hildebrand¹⁸ in his solubility studies. The value for its moment reported in this paper is of interest in connection with the study of its solubility relations which have recently been reported by that author with one of his collaborators.¹⁸

AgClO₄.—The solubility relations of this interesting substance in benzene have been studied by Hill.¹⁹ This author states that a molecular complex, AgClO₄·C₆H₆, is formed when AgClO₄ is added to benzene. The value found for the moment of this molecule is very large; nevertheless it is believed to be significant. As in the case of the iodine the molar polarization-mole fraction curve is a straight line over the range of concentration studied, again indicating the elimination of possible chemical interference.

Summary

1. Dielectric constant and density data have been obtained for benzene solutions of benzoic acid, phenol, iodine, stannic iodide, antimony triiodide and silver perchlorate.

2. By means of the Debye modification of the Clausius-Mossotti Law these data have been used to calculate the electric moments of the various solute molecules.

3. The results of these calculations have been discussed with particular reference to the conceptions of atomic structure and to solubility relationships.

MADISON, WISCONSIN

¹⁸ Dorfman and Hildebrand, *THIS JOURNAL*, **49**, 729 (1927).

¹⁹ Hill, *ibid.*, **44**, 1163 (1922). This article gives references to previous papers.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE POTENTIAL OF A PROPOSED STANDARD FORM OF COPPER AND THE ACTIVITY OF COPPER SULFATE¹

BY RALPH F. NIELSEN AND DENTON J. BROWN

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This research was undertaken in connection with the attempt to find a standard form of copper for use in potential measurements involving various compounds of copper. The potential of the copper electrode in copper sulfate solution has been measured by numerous investigators, using various forms of copper, and the results always depended on the method of preparing the electrodes. Lewis and Lacey² give the value 0.3928 volt for the electromotive force of the cell $\text{Cu} \mid \text{CuSO}_4(0.05 \text{ } M) \mid \text{Hg}_2\text{SO}_4 \mid \text{Hg}$, using a copper sponge prepared by rapid electrolysis of copper sulfate on a platinum point. They found a considerable number of cells to agree within several tenths of a millivolt, using various current densities in preparing the copper. We have been unable to obtain reproducible results using copper prepared by their method, and invariably the copper lost its reducing activity slowly upon standing under concentrated copper sulfate solution. The following table gives the relative potentials of a sample of copper prepared by this method at the time indicated.

TABLE I
RELATIVE POTENTIALS

Day.....	11/19/26	11/23/26	11/29/26	12/3/26
E.m.f.....	0.1595	0.1551	0.1531	0.1523

In addition, pieces of wire and sheet were heated to a temperature near the melting point of copper in an atmosphere of nitrogen and slowly cooled. These gave values somewhat lower, although we could not obtain constant results. These facts are in agreement with a rather generally accepted theory that metals freshly precipitated by violent reduction are abnormally high in their reducing power. In fact, a copper sponge obtained by the action of zinc dust on copper sulfate solution gave exceptionally high values. All our values were admittedly higher than those of Lewis and Lacey, but we can see no reason why their values should be selected as standard.

It became necessary to find a form of copper which gave constant results that could easily be reproduced by any investigator, and we finally

¹ This paper is an abstract of part of the work done by Ralph F. Nielsen toward the degree of Doctor of Philosophy at the University of Nebraska. The problem of the determination of free energies of copper compounds was selected by him at the suggestion of Professor Merle Randall of the University of California, and the work of this paper was found necessary in carrying out the problem.

² Lewis and Lacey, *THIS JOURNAL*, 36, 804 (1914).

decided to use a two-phase electrolytic amalgam in our work. By accurately determining the standard potential of this form of copper, we can easily correct our subsequent data on various copper compounds when a justifiable standard form of copper is found. We made a number of measurements involving copper sulfate solution, making use of this amalgam. The copper amalgam was prepared by electrolysis of a half-molal solution of copper sulfate, slightly acidified, using about five amperes per square decimeter of mercury surface and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis of a 25% solution of sulfuric acid, using about five amperes to a square decimeter and a rapid stirrer which just grazed the mercury surface, according to the method of Hulett.³ The copper sulfate used had been recrystallized from an acidified solution of the best c. p. crystals obtainable, and the solutions were made up gravimetrically from a stock solution standardized iodimetrically with metallic copper as primary standard. Molality is taken as moles per kilogram of water in vacuum. Conductivity water and distilled mercury were used in preparing the reagents. Measurements were made on a Leeds and Northrup "Type K" potentiometer, using a new Weston cell with a Bureau of Standards Certificate. The thermostat consisted of a bath of distilled water maintained at $25 \pm 0.05^\circ$. The mercurous sulfate electrodes were always placed in glass-stoppered flasks, rotated in the thermostat for several hours and then put into dry electrode vessels of the usual type. All heating and regulating circuits were shut off during the measurements and all connections were made by means of mercury. We measured the following cells, each value being the mean of four different cells, none deviating more than a tenth of a millivolt from the mean. The four cells were obtained by cross combinations among two electrodes of each kind.

TABLE II
CELL MEASUREMENTS

Cu (amalgam)	CuSO ₄ (0.05 M)	Hg ₂ SO ₄	Hg	0.3874 volt
Cu (amalgam)	CuSO ₄ (0.1 M)	Hg ₂ SO ₄	Hg	.3784 volt
Cu (amalgam)	CuSO ₄ (0.2 M)	Hg ₂ SO ₄	Hg	.3697 volt
Cu (amalgam)	CuSO ₄ (0.4 M)	Hg ₂ SO ₄	Hg	.3592 volt

The cell Cu(amalgam) | CuSO₄(sat.) | Hg₂SO₄ | Hg has been measured by Cohen, Chattaway and Tombrook,⁴ by Obata⁵ and by Öholm⁶ using reagents prepared as above. The mean value from the last two investigators is 0.3467 volt \pm 0.0001. As a check on our preparations we re-

³ Hulett, *Phys. Rev.*, **32**, 32 (1900).

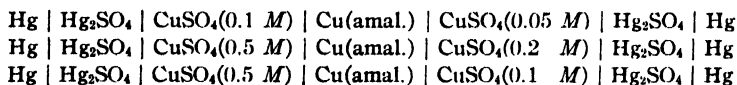
⁴ Cohen, Chattaway and Tombrook, *Z. physik. Chem.*, **60**, 706 (1907).

⁵ Obata, *Proc. Phys. Math. Soc. Japan*, [3] **2**, 223 (1920).

⁶ Öholm, *Medd. Vetenskapsakad. Nobelinst.*, **5**, N:04, 1 (1919).

peated these measurements and obtained $0.3468 \text{ volt} \pm 0.0001$. Since we were afraid that we had not washed all the acid from the crystals of copper sulfate before making up our solutions, we recrystallized some from a neutral solution and repeated the measurements at $0.2 \text{ } M$ concentration. We obtained perfect agreement, however, with the above. Since we found that we could not avoid the formation of a green precipitate at the mercurous sulfate electrode in the case of the $0.05 \text{ } M$ solution, this solution contained a drop of nitric acid in a liter of the solution. This should not affect the activity coefficient noticeably if the degree of hydrolysis is small; and, indeed, it was found to have no effect in the $0.1 \text{ } M$ solution. We did not think it advisable to carry these measurements into more dilute solutions owing to the solubility of mercurous sulfate.

As a further check on our activity coefficients we combined our electrodes in the following way,



These cells gave, respectively, $0.0089 \text{ volt} \pm 0.0001$; $0.0105 \text{ volt} \pm 0.0001$; $0.0190 \text{ volt} \pm 0.0001$.

Employing the values of the two tables, we obtain the following series of activity coefficients:

TABLE III					
ACTIVITY COEFFICIENTS					
M	0.05	0.1	0.2	0.5	1.38
γ216	.153	.107	.064(4)	0.0378

The value of 0.216 for the $0.05 \text{ } M$ solution was taken from Lewis and Randall.⁷ These values are about three per cent. lower than theirs, but are undoubtedly more nearly correct, since their calculations from freezing point measurements were not corrected for the heat of dilution.

For the standard potential of copper amalgam we obtain -0.3502 volt , based on the mean activity of the ions in copper sulfate solution. The copper amalgam used above seems to be a good standard form of copper for use in potential measurements. It is easily reproducible and, since it is a two-phase amalgam, its potential is independent of the relative quantities of copper and mercury within rather wide limits. The General Electric Company has prepared single, unstrained crystals of copper, and we attempted to obtain some from them, to see if they would give the same potential as the amalgam. They had none on hand, however, which had not been strained, so we did not perform this experiment.

⁷ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, 1923.

Summary

The choice of a standard form of copper for use in potential measurements was discussed.

The standard potential of copper amalgam and the activity coefficients of copper sulfate over a limited range were determined.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA,
No. 42]

THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC GOLD¹

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Introduction

In a previous communication³ evidence was presented to show that the mechanism of water formation over a reduced silver catalyst involves collisions of gaseous hydrogen with adsorbed oxygen on that fraction of the surface not covered by adsorbed water. In this case the reaction kinetics proved to be relatively simple.

Metallic gold like metallic silver does not form definite compounds by direct combination at ordinary pressures with either hydrogen or oxygen.⁴ Their similarity in chemical properties would lead one to expect that the reactions in contact with the two metals would exhibit similar kinetics and mechanism. The present investigation shows that this is not the case, although the adsorption phenomena for the two metals are similar.

Bone and Wheeler⁵ have studied the hydrogen-oxygen combination in contact with gold gauze at 250° by a circulatory method. They state that the results for gold and silver were analogous; namely, that the rate of reaction was roughly proportional to the pressure of hydrogen, but independent of the pressure of oxygen, and that the activity of the catalyst was greatly stimulated by previous heating in hydrogen but not in oxygen. This latter effect was further investigated by Chapman, Ramsbottom and Trotman.⁶

The experimental method and the conclusions of Bone and Wheeler have been discussed and criticized in other places.³ The difficulties

¹ Presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society held at Richmond, Virginia, April 11-16, 1927.

² Du Pont Fellow in Chemistry during the period covered by this investigation.

³ Benton and Elgin, *THIS JOURNAL*, **48**, 3027 (1926).

⁴ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, 1923, Vol. III, pp. 525-526, 577.

⁵ Bone and Wheeler, *Phil. Trans.*, 206A, 1 (1906).

⁶ Chapman, Ramsbottom and Trotman, *Proc. Roy. Soc. (London)*, 107A, 29 (1925).

inherent in the manometric method of measuring contact catalytic reactions were avoided in the present study by use of the flow method, which allowed the attainment of a "steady state" under each set of conditions. The kinetics of the reaction have been accurately determined, the adsorptions of hydrogen and oxygen by the gold catalyst measured and an attempt made to deduce a mechanism for the catalytic reaction.

Experimental Method

Apparatus.—The apparatus was the same as that employed in the investigation of the reaction in contact with metallic silver. Suitably purified gas mixtures were passed over the catalyst maintained at constant temperature in an electric furnace, and the progress of the reaction was followed by weighing the water absorbed in a calcium chloride tube from the exit gases during time intervals of five minutes.

Preparation of the Catalyst.—A 6% solution of C. P. gold chloride was heated to 80° and a slight excess of a 6% solution of sodium carbonate added with constant stirring. The mixture was then heated to boiling for thirty minutes. The precipitated gold hydroxide was washed repeatedly by decantation, then filtered off and the washing continued until no chloride could be detected in the wash water. The layer next to the filter paper was discarded, and the remainder dried in an oven at 100°.

The hydroxide was reduced in a current of dried hydrogen. The reduction was started at about 5°, but the temperature increased slowly as reaction proceeded. The temperature was maintained at 35° for fifteen hours, after which it was slowly raised to 100° and maintained until no water could be detected in the exit gas.

The reduced gold thus obtained was placed in the catalyst furnace and heated in a stream of dry oxygen at 200° for two hours. This sample of gold was used throughout the experiments, and gave detectable conversion at 100°. It was 2.1 cm. in diameter and approximately 2 cm. high, giving an apparent volume of 7 cc. Its weight was 8.78 g.

Procedure.—The procedure used with silver was followed. The uniform preliminary treatment of the catalyst with hydrogen for an hour previous to each run was made at 130°. The total rate of flow was maintained constant at 50.0 cc. (0°, 760 mm.) per minute throughout the experiments.

Check runs were made alternately throughout the investigation. During the first ten runs no material change in catalyst activity was noted. The small changes which occurred in the later runs were corrected for by adding to or subtracting from the yield in each run the percentage amount per run necessary to make the checks agree.

Experimental Results on Reaction Kinetics

One hundred thirty degrees proved to be a convenient temperature at which to investigate the reaction kinetics. The results of typical catalytic runs are shown in Fig. 1, in which the yield of water per five minute interval is plotted as a function of time.

With oxygen in excess the initial course of the reaction could not be followed due to the time required to sweep from the furnace the hydrogen

used in the preliminary treatment. Here attainment of the "steady state" required a much longer time than when hydrogen was present in excess. In the previous work with silver, the "steady state" was always reached within an hour of the start of a run, irrespective of which gas was present in excess.

When hydrogen was used in excess, determinations of the oxygen present in the exit gas showed that the rate at which oxygen disappeared was equivalent to the rate of water formation. This fact indicates that oxygen was not continuously taken up and retained by the catalyst in any considerable amount. From experiments with oxygen in excess, a similar conclusion was drawn in regard to hydrogen.

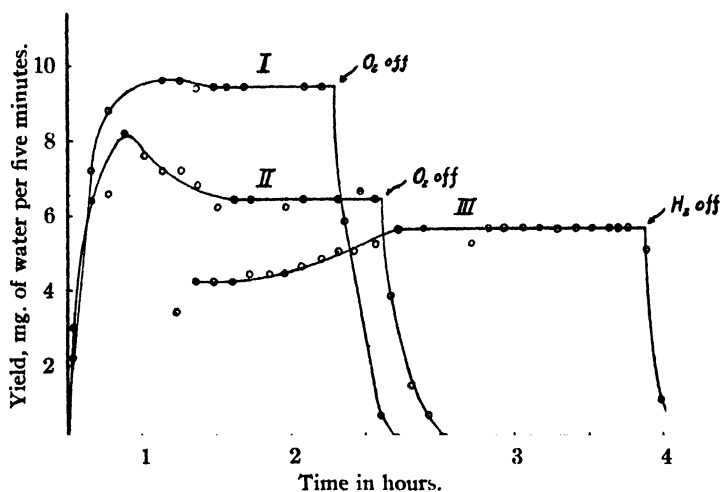


Fig. 1.—Variation of yield with time in typical runs. Curves I (Run 7) and II (Run 6) are with excess hydrogen, and oxygen equivalent to 40.4 and 20.2 mg. of water per five minutes, respectively. Curve III (Run 12) is with excess oxygen, and hydrogen equivalent to 40.4 mg. of water per five minutes.

With constant total flow rate the influence on the yield of oxygen pressure, hydrogen pressure and temperature, as well as the effect of water vapor and of preliminary treatment of the catalyst with oxygen, have been studied.

Effect of Oxygen Pressure.—To determine the effect of oxygen pressure on the rate, experiments were made at 130° with excess hydrogen and with amounts of oxygen equivalent to from 10 to 100 milligrams of water per five minutes. The average partial pressures corresponding to these quantities may be seen in Table I. In order to keep the flow constant and at the same time vary the oxygen pressure, the flow of hydrogen was suitably adjusted to allow for variations in the volume of oxygen introduced. The average hydrogen pressures, therefore, vary

slightly, but due to the excess of hydrogen this does not exert a marked influence upon the yield, as will be shown below. The variation is taken care of quantitatively in the final equation summarizing the kinetic results.

TABLE I
EFFECT OF OXYGEN PRESSURE ON THE YIELD

Run no.	Total flow rate, 50 cc. per minute.		Temperature, 130°		Yield, mg. of water per five minutes	
	Oxygen, cc. per min.	Barometer, mm.	Av. hydrogen press., mm.	Av. oxygen press., mm.	Calcd.	Obs.
5	5.02	745.7	661.6	66.7	40.4	9.2
6	2.51	749.9	706.0	31.7	20.2	6.4
7	5.02	749.0	664.2	66.8	40.4	9.4
8	1.25	750.1	727.0	15.8	10.1	4.6
9	5.02	756.0	670.5	67.1	40.4	9.3
10	12.55	757.0	551.9	180.1	101.0	13.0

These experiments show that the rate of the reaction in contact with gold, unlike the case of silver, is a function of the oxygen pressure. Although the yield appears to be approximately proportional to the square root of the oxygen pressure under these conditions, the true relation can be found only by taking into consideration the effect on the yield of the varying quantities of water vapor produced. This effect forms the subject of a later section.

Effect of Hydrogen Pressure.—The influence of hydrogen pressure was next investigated, using small hydrogen concentrations in excess oxygen. Quantities of hydrogen equivalent to 10 to 100 milligrams of water per five minutes were used. The alternate check runs showed a gradual change in activity during the series. Run 16 was chosen as the standard since this seemed best to represent the state of activity existing in the series with excess hydrogen. The yields of the present runs have been corrected to this standard by adding or subtracting the required amounts in the manner previously indicated. Run 19 was used in relating the results of Tables I and II. The corrected yields of runs 5

TABLE II
EFFECT OF HYDROGEN PRESSURE ON THE YIELD

Run no.	Total flow rate, 50 cc. per minute.		Temperature, 130°		Yield, mg. of water per five minutes		
	Hydrogen, cc. per min.	Barometer, mm.	Av. oxygen press., mm.	Av. hydrogen press., mm.	Calcd.	Obs.	Corr.
12	10.04	743.7	593.8	139.4	40.4	5.6	5.0
13	5.02	746.6	671.7	69.7	20.2	2.8	2.6
14	10.04	744.6	594.6	140.3	40.4	5.2	5.0
15	2.51	744.0	706.8	34.7	10.1	1.4	1.4
16	10.04	746.7	595.6	141.8	40.4	5.0	5.0
17	25.09	746.6	364.8	360.2	101.0	9.2	9.8
18	10.04	751.8	40.4	4.4	5.0
19 ^a	44.98	748.8	66.9	667.1	40.4	8.6	9.2

^a Excess hydrogen.

to 19 are thus based, as closely as possible, on the same state of catalyst activity. The data obtained for the effect of hydrogen pressure are given in Table II.

From these experiments it is seen that when oxygen is present in large excess the rate of water formation is markedly dependent upon the hydrogen pressure. The apparent proportionality to the first power of the pressure of this gas must be corrected, as in the case of oxygen, for the variations in the pressure of water vapor. Incidentally it may be mentioned that the largest conversion obtained was with an approximately stoichiometric mixture.

Effect of Water Vapor.—A series of five runs was made to determine the effect on the yield of water vapor initially present in the entering gas. The desired concentration of water vapor was added by passing the entering gas through a saturating train containing distilled water at the required temperature. Table III gives the data obtained.

TABLE III
EFFECT OF WATER VAPOR ON THE YIELD

Excess hydrogen. Temperature, 130°. Total flow, including entering water vapor, 50 cc. per minute.

Run no.	Barometer, mm.	Oxygen cc. per min.	Mg. water per 5 min. in entering gas	Mg. water per 5 min. in exit gas	Yield, mg. of water per five minutes	
					Obs.	Corr.
23	743.4	5.02	0.0	9.6	9.6	8.6
24	740.4	5.02	5.6	9.2	3.6	3.4
25	739.9	5.02	0.0	8.6	8.6	8.6
26	743.0	5.02	1.6	10.2	8.6	7.2
27	743.7	5.02	0.0	11.4	11.4	8.6

Water vapor initially present in the reacting gases markedly decreases the rate of water formation. The effect is greater when larger amounts of water are present. However, the retardation in these experiments is not nearly so marked as that observed with silver. This undoubtedly is to be attributed to the higher temperature used in the present instance. The retarding influence exhibited by water vapor can be ascribed to the adsorption of water vapor on the gold surface, which largely prevents contact with the reacting gases.

Temperature Coefficient.—To ascertain the variation of yield with temperature, the run with excess hydrogen and an oxygen concentration equivalent to 40.4 milligrams of water per five minutes was made at several temperatures. Due to increased yield at higher temperatures, the average pressures of hydrogen and oxygen varied somewhat through the series. The yields have, therefore, been corrected to a hydrogen pressure of 660 mm. and an oxygen pressure of 67 mm., using the data previously obtained for the effect of the pressures of these gases. Due to the large excess of hydrogen, the corrections for variation in its average pressure are practically negligible. The results are recorded in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON THE YIELD

An excess of hydrogen was used. Total flow rate, 50 cc. per min.

Run no.	Temp., °C.	Av. hydrogen press., mm.	Av. oxygen press., mm.	Yield, mg. of water per 5 min.		
				Obs.	Corr. for activity	Corr. for activ. and gas press.
19	130	664.6	67.8	8.6	8.6	8.6
20	145	651.2	58.1	19.2	19.2	20.9
21	130	662.3	67.5	8.6	8.6	8.6
22	151	637.9	48.5	29.1	25.7	31.2
23	130	658.8	66.4	9.6	8.6	8.6

If the logarithms of the corrected yields are plotted against the reciprocals of the absolute temperatures a straight line is obtained. The slope of this line when multiplied by -4.58 gives a value of 20,800 calories for the apparent heat of activation (E). This is about 8000 calories larger than the value obtained with a silver catalyst. The actual temperature coefficient for a 10 degree rise is 1.95 for the interval 130–140° and 1.88 for the interval 145–155°. The average temperature coefficient with silver was 1.6.

Effect of Preliminary Heating of the Catalyst in Oxygen.—In the runs made to determine the effect of preliminary treatment of the catalyst with each reacting gas all other conditions were identical. The results are shown in Table V.

TABLE V

EFFECT OF PRELIMINARY TREATMENT OF THE CATALYST

Temp., 130°. Excess hydrogen. Flow rate, 50 cc. per min. Calcd. yield, 40.4 mg.

Run no.	Preliminary heating at 130°		One quarter	Obs. yield, mg. of water per 5 min.		
	In hydrogen, hours	In oxygen, hours		Time from start, hours	One	Two
27	1	11.4	11.4	11.4
28	...	1	26.2	16.0	13.2	...
29	1	...	11.6	12.0	12.8	13.0
30	...	6.5	31.0	23.8	18.6	17.8
31	1	...	16.4	15.2	15.2	...
32	9	...	10.4	11.6	12.8	13.8

These experiments show that the gold is a more active catalyst after preliminary heating in oxygen. The stimulating effect was not lasting, a maximum yield being obtained at first, followed by a gradual decrease toward a normal one after several hours' time. Preliminary treatment with oxygen for six and one-half hours is more effective and enduring than treatment for one hour.

Sieverts⁷ found that gold *absorbs* neither hydrogen nor oxygen under any conditions examined, and the measurements described below show that under the prevailing conditions oxygen but not hydrogen is appreciably *adsorbed*. The effect observed is, therefore, presumably to be con-

⁷ Sieverts, *Z. physik. Chem.*, 60, 179 (1907).

sidered as an increase in yield due to oxygen treatment rather than a decrease due to hydrogen.

The difference between the total quantity of water obtained in a run following treatment with oxygen and that which would be obtained over the same period in a normal run, in which the catalyst was previously heated in hydrogen, was many times greater than the amount equivalent to the volume of oxygen which the subsequent adsorption experiments showed was taken up by the catalyst. The increased yield is not, therefore, simply the conversion of the oxygen adsorbed during the preliminary treatment. The presence of oxygen initially on the surface produces some distinctive influence on the rate of the reaction which gradually disappears as the reaction proceeds.

A proposed explanation of the observed phenomena will be considered in the discussion.

Adsorption Measurements

Apparatus and Procedure.—The adsorption measurements were made by the usual static method. The essential features of the apparatus were a bulb containing the gold connected by 3-way stopcocks to a mercury manometer, a Töpler pump, a gas buret with mercury as retaining liquid and generating and purifying lines for the gases employed.

The adsorptions at each pressure were determined in separate experiments. The bulb was evacuated at the desired temperature (generally 130°) and the gas admitted up to a definite pressure. The pressure change was followed at frequent intervals until it became very small. Occasional readings were then taken until successive ones over about six hours' time were identical, when equilibrium was assumed to have been reached. The volume adsorbed at each pressure was determined by subtracting from the total volume admitted the volume of gas in the free space. The latter was measured with nitrogen, which was assumed not to be measurably adsorbed.

The bulb was evacuated at 130° immediately following an experiment, and the gas pumped off measured. Adsorbed oxygen could not be pumped from the surface at this temperature and it was therefore necessary to burn it off with hydrogen after each measurement. The hydrogen recovered after this process was measured. The amount disappearing was closely equivalent to the volume of oxygen which was found to remain on the surface after an oxygen run.

The sample of gold used in the catalytic experiments was employed. Some of it was lost in transferring to the adsorption bulb so that its weight was reduced to 7.94 g.

Results.—The oxygen adsorption isotherm for 130° is shown in Fig. 2. The results of the measurements are summarized in Table VI.

Attempts were made to measure hydrogen adsorption at 25° on the gold surface covered with adsorbed oxygen, but no adsorption could be detected under such conditions.

The measurements show that considerable quantities of oxygen are adsorbed, but a scarcely measurable amount of hydrogen. Although the hydrogen was quantitatively recoverable, only a few tenths of a cubic centimeter of oxygen could be pumped off at 130° after an experiment

with this gas. It is evident that the adsorption of oxygen at equilibrium is very nearly independent of the pressure.

TABLE VI
ADSORPTIONS BY 7.94 G. OF GOLD

Gas	Temp., °C.	Vol. introduced, cc.	Vol. in free space, cc.	Final press., mm.	Vol. adsorbed, cc.
H ₂	130	28.27	28.17	739.2	0.10
O ₂	130	3.57	0.0	0.0	3.57
O ₂	130	6.95	2.78	74.7	4.17
O ₂	130	20.35	15.75	416.0	4.60
O ₂	130	29.48	24.70	646.2	4.78
O ₂	130	29.46	24.65	650.2	4.81
O ₂	98	32.15	28.58	676.6	3.57
O ₂	157	28.78	23.05	646.0	5.73
O ₂	157	29.46	23.70	657.7	5.76

In the range of the measurements the oxygen adsorption at apparent equilibrium increases with increasing temperature. At about 650 mm. pressure the gold took up 3.57 cc. at 98°, 4.78 cc. at 130° and 5.73 cc. at 157°. At first glance these results would seem to indicate a negative heat of adsorption. This conclusion would, however, be justifiable only in case true equilibrium is attained at each temperature. To test this point further, the oxygen adsorption at 130° and 650 mm. pressure was repeated, the measurement being continued for forty-eight hours after apparent equilibrium had been reached. Without removing the oxygen, the temperature was raised to 157° and the system allowed to come to equilibrium. The adsorptions so determined were in agreement with those found in the previous experiments. The temperature was then lowered to 130°. Although this temperature was maintained for eighty hours no decrease occurred in the amount of gas adsorbed. Hence we must conclude that, in spite of the apparent constancy of the pressure, true equilibrium was not attained in the first part of the experiment.

Rate of Oxygen Adsorption.—Typical curves showing the rate of oxygen adsorption at different temperatures and pressures are shown in Fig. 3, in which manometer readings are plotted against the square root of the time, this function being chosen merely for convenience. It will be noted that the rate decreases markedly with decreasing temperature.

adsorbed
of oxy
(0°, 76
m.).

0 100 200 300 400 500 600 700 800
Pressure in mm. of mercury.

Fig. 2.—Oxygen adsorption isotherm at 130°.

Thus at 130° approximately twenty-four hours were required for apparent equilibrium to be established, one hundred and eight hours at 98°, while at 25° only 4 mm. pressure drop, corresponding to an adsorption of 0.1 cc. of gas, occurred in seven hours. Curves III and IV of Fig. 3 show that

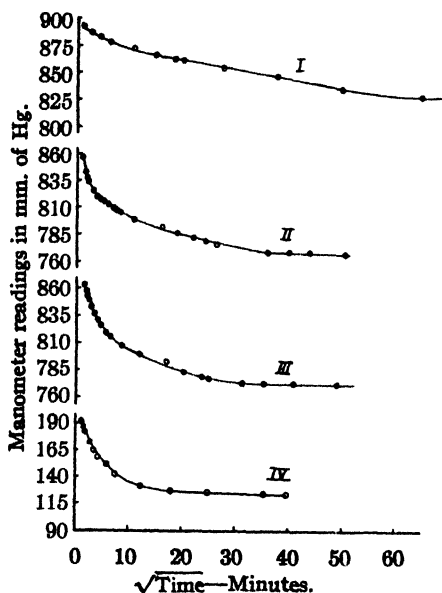


Fig. 3.—Decrease of pressure with time in the adsorption of oxygen. Curve I is for 98° and 752 mm. and Curve II for 157° and 735 mm. pressure. Curves III and IV are for 130° and 776 and 94 mm. initial pressures, respectively.

the rate of adsorption is nearly independent of the gas pressure. During the first minute the rate is slightly higher at the higher pressures, but thereafter no appreciable difference was observed. Experiments at intermediate pressures, not shown in Fig. 3, confirm these results.

In the previous work with silver, slow rates of oxygen adsorption were also encountered, but to a less pronounced degree than in the present experiments with gold. The slow rate of adsorption cannot be attributed to oxidation of the gold in the ordinary sense since it is well established that this metal is not oxidized by oxygen under any conditions. The possibility that the slow disappearance of oxygen is due to solution appears improbable in view of Sieverts' measurements,⁷ which indicate that massive gold does not dissolve

this gas in appreciable quantities at any temperature. It seems necessary to conclude that at least that part of the gas taken up at low pressures, which is the major portion, is in the adsorbed state.

Discussion

Kinetics.—The treatment of the kinetics in flow systems is much simplified by expressing the yield as a function of the average pressures of the various gases instead of employing the more accurate method of integration. We have previously shown⁸ that this approximation is justifiable unless the conversion approaches completion.

Since water vapor markedly retards the reaction, presumably because of extensive adsorption on the catalyst surface, the effect of changes in the pressure of this gas must be included in the consideration of the kinetics,

⁸ Benton, *Ind. Eng. Chem.*, 19, 494 (1927).

It has been shown by Langmuir⁹ that the fraction of a surface not covered by adsorbed gas is given by the expression $1/(1 + ap)$, where p is the gas pressure and a is a constant at a given temperature. For large adsorptions this reduces to $1/ap$. We may, therefore, write for the yield in the reaction under consideration

$$Y = kp_h^m \cdot p_o^n / ap_w$$

where p_h , p_o and p_w are the averages of the inlet and exit pressures of hydrogen, oxygen and water, respectively, k is the reaction-rate constant and m and n are constants to be determined by comparison with experiment. In the present work the rate of flow was maintained constant, and, therefore, p_w is proportional to Y . Hence,

$$Y^2 = k \cdot p_h^m \cdot p_o^n$$

This expression shows that the exponents of the pressures of the hydrogen and oxygen should be twice as great as those which are obtained when the retarding effect of the water vapor is neglected. Since the results of Tables I and II indicate that the apparent exponents are unity and 0.5, respectively, before correcting for the effect of the water, the true kinetic equation evidently should be

$$Y = k \cdot p_h^2 \cdot p_o / (1 + ap_w)$$

This may be put in the form

$$\frac{p_h^2 \cdot p_o}{Y} = \frac{1}{k} (1 + ap_w) = \frac{1}{k} + k'Y$$

If this relation satisfies the data, the points obtained by plotting $p_h^2 \cdot p_o / Y$ against Y at constant temperature should fall on a straight line. Fig. 4 shows that this is the case for the results of Tables I and II considered separately. It is possible that the failure of the points obtained with excess oxygen and with excess hydrogen, respectively, to fall on the same curve is due to a real difference in kinetics in the two cases, but in view of the uncertainty in the correction of the separate series to the same state of catalyst activity, it is felt that no stress should be laid on this point.

Reaction Mechanism.—It has been shown previously that an active silver catalyst adsorbs oxygen to an extent nearly independent of the pressure, but does not adsorb hydrogen. It would appear reasonably certain, therefore, that during catalysis the active parts of the silver surface are largely covered with adsorbed oxygen under all conditions. In agreement with this result the rate of water formation was found to be independent of oxygen pressure and directly proportional to the pressure of hydrogen. Since a gold catalyst adsorbs the gases in question in a similar manner, it would appear that the kinetics with gold should be similar to those with silver. With gold, however, the yield is proportional to the

⁹ Langmuir, *THIS JOURNAL*, 40, 1370 (1918).

square of the hydrogen pressure and to the first power of the oxygen. Since in both cases the oxygen adsorptions at equilibrium are nearly independent of the pressure, the only basis upon which to explain this difference in reaction kinetics appears to lie in the fact that the *rate* of oxygen adsorption on gold is considerably slower than on silver. More than half of the equilibrium adsorption on silver occurs instantaneously, while less than a quarter occurs thus with gold. Nevertheless, it is evident

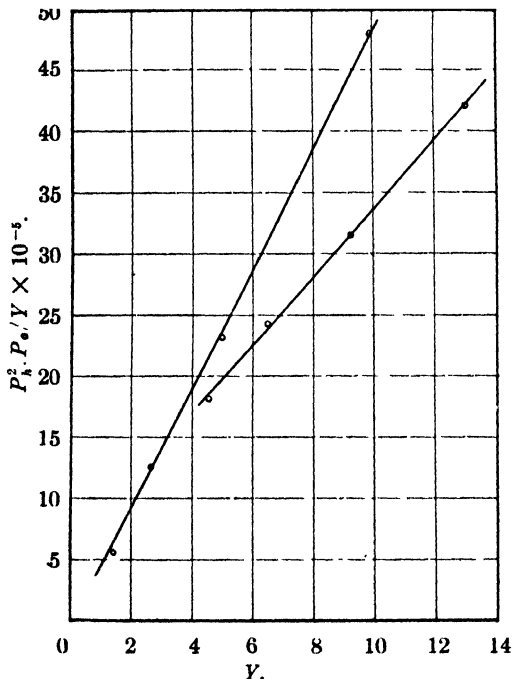


Fig. 4.—The combined effect on the yield of hydrogen, oxygen and water-vapor pressures at constant temperature. Upper curve, Runs 12–18, Table II (with excess oxygen); lower curve, Runs 5–10, Table I (with excess hydrogen).

In view of the much slower rate of adsorption and the shorter time of preliminary treatment of the gold, it is probable that this metal did not become so nearly covered with oxygen during preliminary treatment with this gas as did the silver. This consideration, combined with the hypothesis that only oxygen adsorbed next to a bare space on the surface is readily capable of reaction with hydrogen, would explain the difference in the effect produced on silver and gold by previous oxygen treatment. In one experiment with silver before which it was heated in oxygen for a

that this explanation alone is inadequate to account for all the facts, since the rate of adsorption of oxygen by gold is almost entirely independent of the pressure.

The possibility exists that the rate of adsorption which is of importance in the catalysis may differ from the rates here measured. This could be true if the oxygen which is active catalytically forms only a small fraction of the total oxygen which is adsorbed. It is not improbable that the catalytically active centers are to be identified with the fraction of the surface which exhibits an intermediate adsorptive activity, as suggested by Beebe.¹⁰ This point should be capable of experimental proof by a study of the adsorptions and kinetics over a catalyst poisoned under carefully controlled conditions.

¹⁰ Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

shorter time and at a lower temperature, the yield was increased in the same manner that was found in the case of gold.

It does not seem possible to deduce a reaction mechanism from the present experiments which will offer a satisfactory explanation for the dependence of the yield upon the square of the hydrogen pressure. A mechanism based on the interaction of adsorbed oxygen with two hydrogens adsorbed on adjacent spaces on the catalyst surface will not account for the observed kinetics, since it may readily be shown that with the relative adsorptions found for the two gases this assumption requires the velocity of reaction to be proportional to the square of the hydrogen pressure, but *inversely* proportional to the oxygen. It seems necessary to conclude that the essential mechanism is the collision of gaseous hydrogen with adsorbed oxygen. If it is required that two gaseous hydrogen molecules strike adsorbed oxygen simultaneously for reaction to occur, dependence on the square of the hydrogen pressure necessarily follows. This offers a possible explanation, but one which is rather unsatisfactory for a heterogeneous reaction of this type, especially in view of the probability that the adsorbed oxygen is at least partially dissociated into atoms.

It is probable that an explanation of the result of Bone and Wheeler that the kinetics were independent of oxygen pressure is to be sought in the higher temperature used by them. At increased temperatures the rate of oxygen adsorption would be greatly increased, so that the catalytically active centers would be largely covered with oxygen under all conditions. This could also explain their result that previous oxygen treatment decreased the rate of combination.

Summary

A study has been made of the catalytic formation of water vapor from hydrogen and oxygen in the presence of a reduced gold catalyst in the temperature range 130–150°, including measurements of the reaction kinetics by the flow method and determinations of the adsorptions of the two gases. The principal results are as follows.

1. The rate of reaction varies as the square of the hydrogen pressure and the first power of the oxygen pressure, and is approximately inversely proportional to the pressure of water vapor. Preliminary treatment of the catalyst with oxygen produces a large but transitory increase in yield. The average temperature coefficient is 1.92.

2. Under the conditions of the catalysis hydrogen is adsorbed by gold in scarcely measurable amount. Oxygen, on the other hand, is strongly adsorbed, the quantity taken up increasing with increasing temperature, but being practically independent of the pressure. The rate of its adsorption is very slow; it is practically independent of the gas pressure and increases with increasing temperature.

In spite of the similarity in chemical properties of gold and silver, the kinetics of the hydrogen-oxygen combination over the two metals show little in common. It appears that no simple mechanism for the reaction in contact with gold is adequate to account for the observed results.

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STUDIES IN PHOTSENSITIZATION. I

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The field of photosensitization by mercury vapor has been extended during the past year to processes which do not involve hydrogen. Dickinson and Sherrill¹ showed that ozone was formed from the collision of excited mercury atoms and oxygen. Since the energy of the quantum corresponding to the 2536.7 Å. line is insufficient to decompose an oxygen molecule, they assumed that the reaction occurred through the collision of an excited and normal oxygen molecule.

Olson and Meyers,² investigating in more detail the reaction between hydrogen and ethylene reported by Marshall and Taylor, have shown that the reaction does not go smoothly to form ethane. Ethylene itself is polymerized, there being at the beginning of the reaction an increase in pressure which falls off again as the polymerization proceeds. They also found that the rate of the hydrogen-ethylene reaction was proportional to the square root of the hydrogen concentration.

Senftleben³ has found that the excited mercury atoms will decompose water vapor. Measuring the change in heat conductivity of water vapor when mixed with varying amounts of hydrogen and oxygen, he found that the change which occurred when water vapor and mercury were illuminated indicated that hydrogen was the sole product in the vapor phase. He, therefore, postulated the formation of hydrogen peroxide which condensed out.

The work here presented has as its object an attempt to broaden the field still further by the development of improvements in light sources for use in photosensitized processes and for general photochemical purposes, and by a study of a number of photosensitized and photochemical reactions. Those investigated are the hydrogenation and polymerization of ethylene and acetylene, the reaction of hydrogen and oxygen to form hydrogen peroxide and the decomposition of water, ammonia, ethylene, ethyl and methyl alcohols, acetone, formic acid, hexane, benzene and

¹ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, 12, 175 (1926).

² Olson and Meyers, *THIS JOURNAL*, 48, 389 (1926).

³ Senftleben, *Z. Physik*, 37, 529, 539 (1926).

ethylamine. A preliminary report on part of this work has already been published.⁴

Apparatus and Methods

The experimental arrangement used at the beginning of this work will be designated as the static system and was modeled directly after that of Taylor and Marshall. It consists of a quartz reaction chamber of about 100cc. capacity joined by capillary tubing to a mercury manometer, gas buret system and oil pump. An electric contact between a sealed-in platinum wire and the mercury in the manometer was used to keep the reaction system at constant volume and the course of the reaction was determined by a change in pressure. A change of 0.5 mm. could be detected. In the photosensitized studies the quartz vessel was immersed in a tank through which water was constantly running, with a vertical Cooper-Hewitt arc of the ordinary type at a distance of about 5 mm. from the vessel. Mercury vapor was furnished by about 1 cc. of mercury placed in the quartz tube. When the purely photochemical reactions were under observation the arc was placed outside the tank and allowed to run hot, the light reaching the reaction system through a quartz window in the side of the tank.

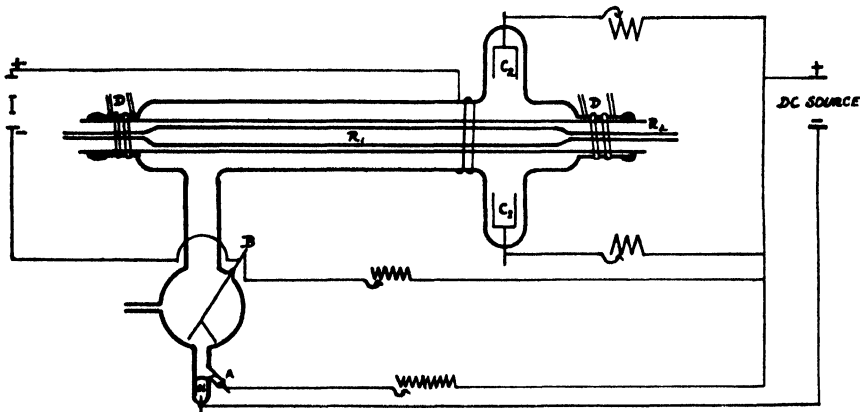


Fig. 1.

The inefficiency of this method was soon quite evident. It had many disadvantages. The arcs, which were run at 10 amperes and 18 volts, deteriorated rapidly. The mercury-vapor pressure in the reaction system could not be controlled independently of that in the arc, which had to be kept low to prevent reversal. Finally, only a very small fraction of the resonance light emitted by the arc could be used in the reaction.

These difficulties were overcome by the development of a cooled mercury arc, based on one used by Langmuir⁵ to study the characteristics of arcs at different vapor pressures. The arc proper is made entirely of G702P Pyrex glass with tungsten leads (Fig. 1). Through the center are two concentric quartz tubes R_1 and R_2 . R_1 is the reaction vessel while R_2 is a water jacket to prevent R_1 from becoming overheated by the action of the arc. The outside glass system is sealed to the quartz by means of rubber composition tape and an outside layer of Gooch crucible tubing, wired and shellacked. This permits operation at 100°. It is advisable, however, to have these seals protected by the two coils of lead pipe D, through which cold water may be kept

⁴ Taylor and Bates, *Proc. Nat. Acad. Sci.*, 12, 714 (1926).

⁵ Langmuir, *Gen. Elec. Rev.*, 27, 538 (1924).

running. N is the negative electrode and A, B, C₁ and C₂ are all positive. N and A are tungsten leads covered with just sufficient mercury to cause the two surfaces to come together on jarring the system. An arc is formed which immediately jumps to B, which is a nickel cone welded to tungsten. This serves the purpose of an electrode and at the same time deflects the mercury vapor from N against the walls of the bulb, which is kept in a water-bath. This regulates the vapor pressure in the arc to that of mercury at the temperature of the bath. The arc can be brought up to electrodes C₁ and C₂ by breaking down the space charge with the induction coil, the secondary of which is shown at I. C₁ and C₂ are two nickel cylindrical electrodes.

The wiring connections are shown in the drawing. The potential necessary depends to a large extent upon the geometry of the arc. In the one in use for this work R₂ is 45 cm. long and 2.5 cm. in diameter; R₁ is 37 cm. long and 1.5 cm. in diameter, the surrounding glass arc being 40 cm. long and 5 cm. in diameter. The side tubes containing C₁ and C₂ are 3.5 cm. in diameter and 5 cm. long. The side tube with the bulb and mercury reservoir is 30 cm. long and 3.5 cm. in diameter, while the diameter of the bulb is 6 cm. This has a drop of 35 volts from C₁ and C₂ to N when running at 18 amperes. The slide wire resistances are of such size and capacity (depending on the voltage of the power source) that the current from A to N is 0.5 ampere, B to N, 5 amperes, and from C₁ and C₂ to N up to 10 each. C₁ and C₂ must have separate resistances or the current would flow entirely to one of them, giving an unevenly distributed discharge. After the arc has been started, electrode B may be disconnected, but A should remain in the circuit to insure a steady arc.

Due to leaks around the seals it was not found feasible to run the arc without a mercury pump in continual operation. If the arc is run with air present in too large quantities, not only do the electrodes become oxidized, causing the arc to emit a pink glow, but the mercury tends to wet the glass between A and N, making it impossible to start. When the arc is first set up or after a long period of disuse the nickel electrodes must be degassed by the passage of a higher current than is ordinarily used.

The temperature of the water in R₂ should if possible be kept above that of the bulb to prevent distillation of mercury from N, which would cut down the light reaching the reaction.

In practice this system has always been used as a means of studying reactions by a flowing method. The gases, before entering R₁, are saturated with mercury at any desired temperature (usually about 50°) by passing them through a glass spiral, in every turn of which is a globule of mercury. In this way the gas passes over 15–20 separate surfaces and is insured of complete saturation. It was by this means that we were able to show that the idea of Rideal and Hirst that the reactions were some sort of catalytic phenomenon in which the mercury surface played a part was erroneous. For the first time the reactions were conducted in the absence of liquid mercury, and yet we obtained rates which were enormously greater than theirs. More concerning the general characteristics and optimum running conditions of the arc will be set forth in that part of this paper which deals with the hydrogen-oxygen reaction.

In the course of these studies it became desirable to do some work involving absorption spectra, for which a fairly intense source of continuous low wave length (2500–1900 Å.) ultraviolet light was necessary. A search of the literature revealed that the best means of producing such light must lie either in a high-frequency discharge under water⁶ or a hydrogen discharge tube.⁷ As ordinarily employed these are not very

⁶ Henri, "Études de Photochemie," Gauthier-Villars et Cie., Paris, 1919, p. 8.

⁷ Tingey and Gerke, *THIS JOURNAL*, **48**, 1838 (1926).

intense and exposures of at least an hour are necessary for spectrographic work.

Attempts to put more energy into an under-water discharge failed, due to the disruptive force of such discharges, which not only make a suitable container difficult to devise, but also cause the spark to emit iron lines as well as the continuous spectrum.

The hydrogen discharge tube yielded better results. This was made of 702EJ Pyrex glass joined at the two points S to 702P to allow the tungsten electrodes to be sealed into the system. These were of 40-mill wire, bent in the form of a spiral with two turns. They are placed 50 cm. apart and in such a position as to allow the light from the discharge to pass through the center of one and out by the quartz window P, sealed on with de Khotinsky cement. The two bulbs were 8 cm. in diameter and the joining tube 5 cm. A 5 kilowatt 110-volt transformer, delivering 25,000 volts on the secondary, was used to excite the discharge. It was run with 60 volts and 140-120 amperes on the primary. The hydrogen pressure was about 17 mm. The tube had to be continuously cooled with a blast of air and could not be run for more than one minute at a time, since it became hot enough to soften and collapse. This, however, was quite sufficient for an exposure, as the accompanying spectrographs (Fig. 5) show.

The lines are mostly those of mercury and a band unidentified. No effort was made to remove them as they are outside the range desired for study and in that region where the more easily obtained tungsten filament serves the purpose.

The Polymerization and Hydrogenation of Ethylene and Acetylene

The work on ethylene was done in the fall of 1925 prior to the publication of Olson and Meyers. It is in entire accord with their observations at low pressures and in some cases makes possible an interpretation of the mechanism involved.

Tank hydrogen purified by passing over hot platinized asbestos and phosphorus pentoxide was used. Tank ethylene, which showed a purity of 99.5% on analysis, was used directly after drying with phosphorus pentoxide. Acetylene was prepared by dropping water on calcium carbide covered with alcohol and was purified by a chain of wash bottles containing concentrated sulfuric acid and solutions of cupric and ferric chloride, mercuric chloride and sodium hydroxide and finally dried over soda lime and by passing through a trap surrounded with carbon dioxide-ether mush. The static system was employed.

The data of a typical run are shown in Table I. The arc was burning at 17 volts and 10 amperes. The alternate jumps of rate at the end of the reaction are due to the inability to read pressure changes to less than 0.5 mm.

Ethylene which had not been subjected to the action of excited mercury gave no test. It will be shown later that hydrogen can also be identified as one of the products.

Returning to the use of the static system, the polymerization of acetylene was investigated. Unlike ethylene, acetylene is polymerized to the yellow solid cuprene both in ultraviolet light and also by excited mercury atoms. The rate of reaction is greater with the cooled arc and the layer of cuprene is heaviest in that part of the reaction system adjacent to the arc, while with the hot arc a more even distribution of the solid is obtained.

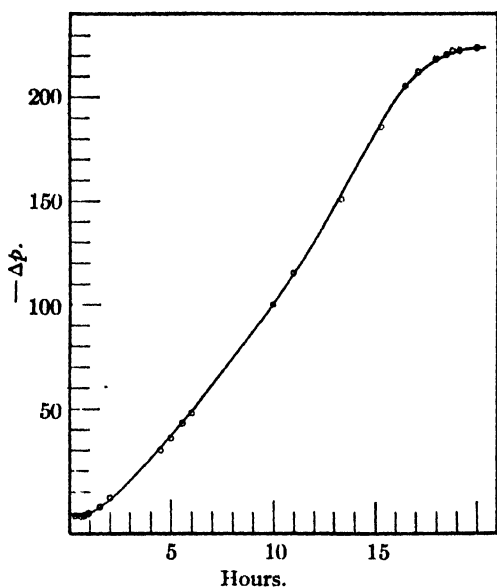


Fig. 3

The layer formed prevents a prolonged run, since it soon cuts down the light intensity and slows down the reaction.

The effect of illuminating a hydrogen - acetylene - mercury mixture with the cooled arc was of much interest. Cuprene was deposited on all portions of the reaction vessel except that adjacent to the arc, which became coated with a colorless oil. The cuprene which condenses in this region is immediately acted upon by the hydrogen atoms. This is a very pretty proof of the fact, known from the work of R. W. Wood⁹ on the absorption of the 2536.7 Å. line by mercury vapor,

that all the activation of mercury atoms occurs in a very thin layer just inside the quartz wall upon which the light falls. In a typical run, 465 mm. of hydrogen and 219 mm. of acetylene were illuminated for thirty hours, giving a final pressure of 412 mm. An analysis of the resulting gases showed from a 32.8cc. sample, 31.4 cc. of hydrogen and 1.4 cc. of unsaturated hydrocarbons. There were no saturated hydrocarbons in the gas phase.

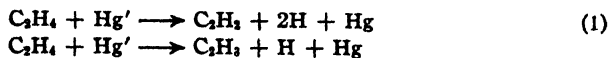
Discussion

The polymerization of ethylene, it can be shown, is the result of an extremely complex series of reactions. The collision of an ethylene molecule and an excited mercury atom very evidently results in the reaction



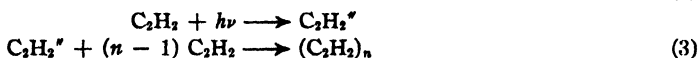
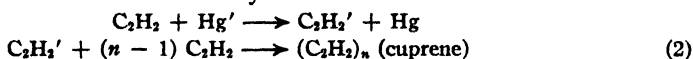
The reactions

⁹ Wood, "Researches in Physical Optics," Columbia University Press, 1913.



are very definitely barred. The first requires 138 kilogram calories. Both, moreover, are not possible because the chances of two hydrogen atoms combining are negligible compared to the probability of formation of a free ethyl group by a collision between a hydrogen atom and the large excess of ethylene molecules present, and experiment shows hydrogen and an increase in pressure, neither of which would be possible under those circumstances.

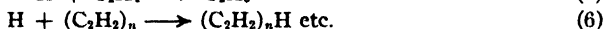
The subsequent reactions which may occur are many, but most of these would be of a second order compared with a particular few. The acetylene may be polymerized in the two ways



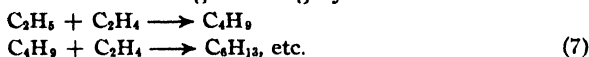
There is also the possibility of the acetylene activated by (2) or (3) reacting in some way with the ethylene. The hydrogen may be dissociated



with the consequent reactions



Unpublished work by Mr. W. H. Jones, mentioned by Taylor,¹⁰ has shown that free ethyl groups, liberated in ethylene, produce reactions which ultimately result in the formation of high-boiling hydrocarbons



Ethyl groups formed in (5) would react in this manner. Our results on the hydrogenation of acetylene show, by the absence of saturated hydrocarbons in the gas phase, that ethane is not formed by the action of acetylene and hydrogen.

These reactions fit in for the most part with the experimental data found on the polymerization. It is to be remarked that not only the primary reaction (1) originates in the narrow zone where mercury atoms in the 2^3P_1 state are present, but also the secondary reactions, with the exception of (3). Olson and Meyers observed that when their arc was allowed to heat up during the initial rise or at any time during the polymerization, no change in pressure occurred. This shows that (3) either does not occur or is of a much lower order of magnitude in the presence of ethylene in large excess. So that, while (1) will be occurring all the time, the subsequent reactions will depend upon the concentrations of hydrogen and acetylene in the zone containing the excited mercury. The initial rise will be regulated by the tendency of these molecules to

¹⁰ Taylor, *Proc. Am. Phil. Soc.*, **65**, 96 (1926).

diffuse away. By a comparison of the initial rise obtained by Olsen and Meyers with ours, we find them to be proportionately greater at low pressures. For example at 0.85 mm. the rise is 0.145, or $\frac{1}{6}$ of the total pressure; at 0.62 mm. it is 0.125, or $\frac{1}{6}$, and at 250 mm. it is 2 mm. or $\frac{1}{180}$ of the original total pressure. This is in accord with the influence of diffusion of acetylene and hydrogen on the initial rise, since the rate of diffusion would vary inversely as the pressure.

The overrunning of the theoretical stopping point in the hydrogenation is also explained by this mechanism. As the concentration of ethylene is increased, the probability of reactions (1) and (7) taking place is increased and so the overrunning is greater.

Hydrogen Peroxide from Hydrogen and Oxygen

Marshall has already reported the formation of hydrogen peroxide as an intermediate step in the photosensitized reaction of hydrogen and oxygen to water, as was predicted from the original chain mechanism postulated for this reaction by Taylor and Marshall. With the development of the new type of arc, giving sufficient energy to employ the flowing method which is necessary for the study of formation of hydrogen peroxide, we have investigated the conditions which favor its production.

Tank hydrogen and oxygen were passed through a tube containing phosphorus pentoxide, saturated with mercury as has been described and then passed through the arc. Hydrogen peroxide was frozen out in a trap surrounded with carbon dioxide snow and ether and titrated against 0.1 *N* potassium permanganate. The rate of flow of the two gases was determined by two water flow meters, calibrated over the desired range.

Preliminary experiments showed that the hydrogen peroxide was due entirely to the mercury present, and was not formed if the gases were sent through the arc without being saturated with mercury vapor. Ozone, however, was present in both cases, as was determined by bubbling the products through a potassium iodide solution, and by the odor. This showed that ozone was not the agent which produced the peroxide.

In Table III is given a summary of the results which show that it is possible to obtain hydrogen peroxide as the sole product by having a fairly rapid rate of flow and an excess of hydrogen.

TABLE III
FORMATION OF HYDROGEN PEROXIDE

Rate of flow, liters per hour		Time of run, min.	Mg. total product	KMnO ₄	Mg. H ₂ O ₂	H ₂ O/Hg
H ₂	O ₂					
100	50	10	..	4.1	7.2	82
60	29	10	6	3.5	6	113
101	28	16	7	4.3	7.3	157
19	11	22	6	0.85	1.5	37
14	51	20	5	.38	0.5	8

The arc was run at 13 amperes with the surrounding bath at 17°. The temperature of the saturator was 25°. The total products were found by weighing and the hydrogen peroxide was calculated from the titration. In the final column are the ratios of mercury atoms entering the system to hydrogen peroxide molecules formed. It can be seen from this that the efficiency of the mercury decreases with increasing oxygen concentration and either too high or, especially, too low rates of flow.

By increasing the temperature of the saturation by mercury a much higher yield of hydrogen peroxide was obtained. In these runs, however, it was found impossible to make any satisfactory measurements of the ratios of total products to hydrogen peroxide.

TABLE IV

FORMATION OF HYDROGEN PEROXIDE AT INCREASED TEMPERATURE OF SATURATION BY MERCURY

No.	Rate of flow, liters per hour		Temp. of bath, °C.	Cc. of 1 N KMnO ₄	Mg, H ₂ O ₂	H ₂ O ₂ /Hg
	H ₂	O ₂				
1	99	49	17	34.7	59	95
2	93	48	17	51.5	82.4	115
3	120	55	17	42.4	67.8	76.8
4	118	54	17	43.5	69.6	78.9
5	49	26	17	37.5	60.0	206
6	48	26	17	35.2	56.4	199
7	102	10	17	67.5	113.7	258
8	100	10	17	38.7	61.9	145
9	100	50	1	29.6	47.3	73.9
10	100	50	1	25.7	41.2	70.7
11	97	50	17	58.4	93.5	164
12	94	49	18	44.0	70.4	127
13	97	49	30	38.6	61.8	109
14	96	49	40	23.5	37.6	67
15	93	49	45	18.6	29.8	54

The arc was operated at 35 volts, 18 amperes, with the mercury saturation at 50°. Each run lasted 10 minutes. In Run 15, with the bath at 45°, the arc became constricted.

In all of these experiments the mercury appeared at the end of the reaction tube, just beyond the illuminated area, in the form of the oxide. Practically no oxide was deposited in the reaction vessel proper. The large number of hydrogen peroxide molecules formed per mercury atom entering shows that each atom is activated many times in passing through the illuminated zone. In Run 7, where the ratio of hydrogen peroxide to mercury is 258, each mercury atom must absorb and transfer at least 43 quanta, according to Marshall's measurements, which shows 6 molecules formed for every quantum absorbed. The atoms can be shown to have been in the illuminated zone two seconds in this run, which gives a time interval of 0.04 second between activations. This is enormously

larger than the value usually assigned to the life of an excited mercury atom in the 2^3P_1 state (10^{-2} sec.). These facts, however, show that the formation of the mercuric oxide is a secondary effect, probably due to the decomposition of the peroxide on the mercury. The non-reproducibility of the results may be accounted for by this, and by photochemical decomposition of the peroxide.

The last seven runs illustrate the efficiency of the arc at various vapor pressures of mercury and very clearly indicate the range of $10\text{--}20^\circ$ as the best operating temperature.

Photosensitized Decompositions

The dissociation of ethylene into hydrogen and acetylene very naturally led to an examination of the possibilities of other such processes brought about by excited mercury atoms. Water, ammonia, ethylene, methyl and ethyl alcohols, hexane, benzene, acetone, formic acid and ethylamine were all decomposed and those products of decomposition which passed through a liquid-air trap analyzed. No substance studied was unaffected by the excited mercury.

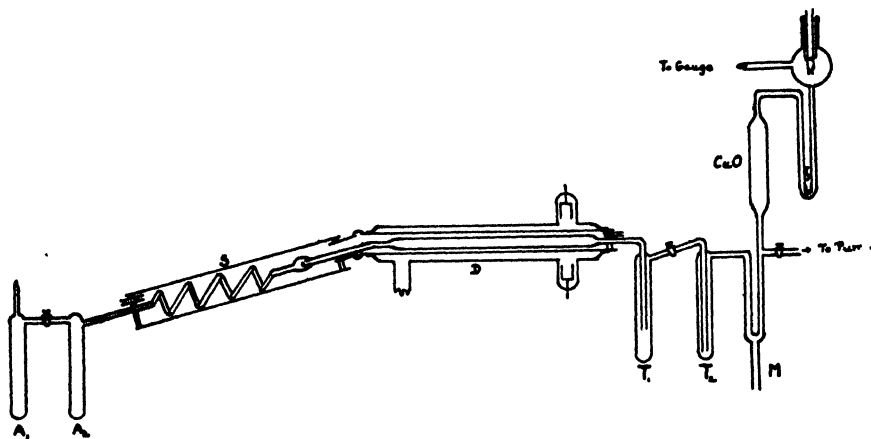


Fig. 4.

The experimental arrangement is shown in Fig. 4. The substance under examination is placed in A_1 and vacuum distilled to A_2 . A_1 is cut out by the stopcock and with liquid air around A_2 and the arc running the whole system is pumped down until the McLeod gage reads about 10^{-5} mm. The pump is then shut off and traps T_1 and T_2 are cooled in liquid air. The substance is then distilled over with the arc not running, as a blank, and the pressure read. This is necessary as some of the materials studied dissolve appreciable quantities of gas at liquid air temperatures. By distilling and pumping out, however, it is possible to obtain only very small pressure increases upon subsequent distillations. The largest

of these is of the order of 10^{-3} mm., which is negligible in comparison with those obtained by the decompositions. The arc is then started and the substance again distilled. The distilling gas is saturated with mercury in the spirals and after passing through the arc all condensable material taken out at T_1 and T_2 , the remaining gases being collected in the bulb of the gage. A run lasted, usually, for about 10 minutes. The pressure is recorded at frequent intervals, at first on the McLeod gage, and then on a side tube reading higher pressures. The gases which pass through the liquid air are nitrogen, oxygen, hydrogen, carbon monoxide and methane. These can be analyzed by means of the platinum filament and copper oxide tube. The mercury cut off at M is raised and the trap T_3 immersed in liquid air. The glowing filament will cause a decrease in pressure if there is oxygen present, but in the presence of methane and no oxygen there is a slight increase, due to the decomposition of the hydrocarbon. This increase was thus a useful indication of the absence of air. When there is such an increase, or when a decrease occurred to a constant pressure, the filament is turned off and the copper oxide heated. Carbon monoxide, hydrogen and methane are thus removed and the residual gas (in the case of ammonia and ethylamine) assumed to be nitrogen. The relative amounts of carbon dioxide and water in the products of combustion can be found by replacing the liquid air around T_3 by carbon dioxide snow and again reading the pressure.

When a comparison is desired between the photosensitized and photochemical reactions the mercury saturator is removed and the whole system cut down and cleaned with nitric acid to remove mercury. The pumping is then carried out for four or five hours through a liquid-air trap which prevents any diffusion of mercury vapor back to the reaction system.

The following typical data from two runs illustrate the method.

AMMONIA—saturated with mercury at 50°		FORMIC ACID (Hg at 50°)	
	Pressure in mm. of Hg		Pressure in mm. of Hg
5 minute blank run with arc off	2×10^{-4}	10 minutes blank	3×10^{-4}
arc running		arc running	
1 minute	0.55	1 minute	3.5
3 minutes	2.3	3 minutes	10.8
5 minutes	3.9	6 minutes	24.4
8 minutes	6.1	arc off	
10 minutes	7.8	Filament	24.4
arc off		CuO	0.7
Filament burning ten minutes	7.8	Changing liquid air to CO ₂	
Copper oxide tube heated two hours	0.87		17.8

A summary of the results is presented in Table V. The pressures recorded are those resulting from a ten-minute run.

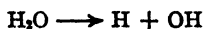
Water Vapor.—The appearance of oxygen in our products of decompo-

TABLE V
COMPARISON OF PHOTOCHEMICAL AND PHOTOSENSITIZED RATES

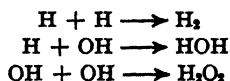
Subs.	Residual gas with- out Hg vapor, mm.	Gas anal., %	Residual gas with Hg vapor, mm.	Gas anal., %	Ratio of photoen- sitized to photochemical rate
H ₂ O	None		1.2	H ₂ , 73; O ₂ , 27	
NH ₃	0.04	H ₂ , 96; N ₂ , 4	7.8	H ₂ , 89; N ₂ , 11	200:1
C ₂ H ₄	None		24.1	H ₂ , 88; CH ₄ , etc., 12	...
CH ₃ OH	0.03		18.0	H ₂ , 58; CH ₄ + CO, 42	600:1
C ₂ H ₅ OH	.7		38.0	H ₂ , 46; CO + CH ₄ , 54	50:1
C ₆ H ₁₄	.016		17.0	H ₂ , 96; CH ₄ , 4	1000:1
C ₄ H ₈	.01		0.3	H ₂ , 60; CH ₄ , 40	30:1
(CH ₃) ₂ CO	4.7	CO + CH ₄ , 100	9.6	CO + CH ₄ , 100	2:1
HCOOH ^a	0.06	...	24.4	CO, 76; H ₂ , 24	400:1
C ₂ H ₅ NH ₂	.34	N ₂ , 4; H ₂ , 96	20.4	H ₂ , 96; CH ₄ , 3.7; N ₂ , 0.3	60:1

^a Six minutes' operation.

sition is probably due to the flowing method used. Senftleben, who found only hydrogen in his reaction vessel after decomposition, was employing a static system, and ozone formed either by low wave length light or excited mercury is known to attack mercury to give the oxide. This does not preclude the possibility of the formation of hydrogen peroxide as an intermediate step. Senftleben has pointed out that the only initial process of decomposition possible with the energy obtained from a quantum of 2536.7 Å. is the dissociation of a water molecule into a hydrogen atom and an hydroxyl group.



The secondary reactions



are all equally probable and not all water molecules originally dissociating would result in the formation of hydrogen and hydrogen peroxide. This fits in with our results in that the efficiency of the mercury in dissociating water is low compared with the other processes, with the exception of benzene. A test of the products contained in the trap showed no hydrogen peroxide, but any condensing there would be immediately decomposed by the mercury present.

The fact that there is an excess of hydrogen (73%) over stoichiometric proportions (67%) can be explained as being due to the same processes which caused Senftleben to obtain no oxygen at all.

Ammonia.—The results on the photochemical and photosensitized decompositions of ammonia are the most important observed in these studies. As can be seen from the table the ratio of the photosensitized to photochemical rates is 200:1, showing that decomposition of ammonia is brought about by energy equivalent to a quantum of wave length 2536.7 Å.

Furthermore, in both types of reaction there is present in the product an excess of hydrogen over stoichiometric proportions (75%). This points to the formation of an intermediate compound such as hydrazine which is removed by the liquid air. The condensate in one of our runs of long duration was tested with a solution of silver nitrate after the ammonia had evaporated off. A black precipitate insoluble in an excess of ammonia was obtained. The reason for the presence of more hydrogen (96%) in the photochemical reaction products than in the photosensitized process (89%) is probably explained by Dickinson and Mitchell¹¹ who published a note on ammonia decomposition simultaneously with our original report. Using a static system, they obtained these same differences to a greater extent (87 and 70%) and explained them by the clean-up effect shown by hydrogen which has been dissociated by the action of excited mercury. This clean-up would naturally be greater in a static system than in one in which gases were continuously flowing.¹²

These new facts make possible a better conception of the mechanism of the photochemical decomposition of ammonia than has been given heretofore. Warburg¹³ measured the quantum yield and found it to be 4 quanta per molecule for light of wave length 2025–2140 Å. Kuhn¹⁴ has made, more recently, a very comprehensive study of the reaction, measuring quantum yields for various temperatures, pressures and wave lengths. Using the same interval of the spectrum as did Warburg, he obtained a yield of 2–2.5 $h\nu$ /mol. for 20°. If he increased the temperature, the efficiency of the light rose also, till at 500° the yield was 0.3 $h\nu$ /mol. The velocity increased proportionally with the quantum yield, being 9 times as great at 500° as at 20°. This temperature coefficient, which amounts to about 50% for every 100° does not obey the ordinary Arrhenius equation but remains constant with $(K_T + 10)/K_T = 1.05$ over the whole range studied. The reaction is independent of the pressure between 5 mm. and 900 mm. Using only the line at 2063 Å. he found that the quantum yield decreased to 10 $h\nu$ /mol. He showed, further, that the reaction rate became smaller as the decomposition proceeded, due apparently to the hydrogen formed, which has a very strong retarding effect on the reaction. Nitrogen was without effect. From these facts he derived a mechanism which not only does not account for the intermediate

¹¹ Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

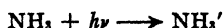
¹² The presence of larger percentages of hydrogen in our reaction products than in those of Dickinson and Mitchell is probably due to our use of a flowing method. In a static system the intermediate products would remain in the illuminated zone and would be further decomposed to nitrogen and hydrogen, while in a flowing system they are immediately removed from the illuminated area and condensed in the traps.

¹³ Warburg, *Sitzb. preuss. Akad. Wiss.*, 1911, 746; 1912, 216.

¹⁴ Kuhn, *Compt. rend.*, 177, 956 (1923); 178, 708 (1924); *J. chim. phys.*, **23**, 521 (1926).

product found by us, but which is also impossible according to the latest available values for the heats of dissociation of hydrogen and nitrogen.

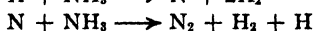
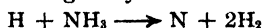
Kuhn assumed that following the absorption of a quantum by a molecule



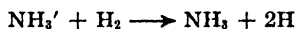
the activated molecule might return to the normal state by reëmission or react according to one of the following equations



However, the first of these is endothermic to the extent of 63,000 cal., if we accept the values of 260,000 cal. and 100,000 cal. for the heats of dissociation of nitrogen and hydrogen. He further suggests that the reason for the high quantum yields at elevated temperatures is the formation of hydrogen and nitrogen by this reaction



This is in direct contradiction to his explanation of the slowing up of the reaction in the presence of hydrogen, which he says is caused by the activated ammonia molecules dissociating hydrogen molecules by collisions of the second kind

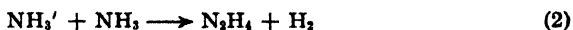


The fact that the quantum of 112,000 cal. will decompose ammonia shows that there is necessary no additional activation other than the absorbed quantum which is equivalent to 128,000 cal. The molecules reacting have the same energy as the average energy of all the molecules. This is further demonstrated by the fact that the temperature coefficient remains constant. The explanation of the low quantum yield by assuming reëmission of the light by some of the molecules before reaction can take place does not agree with the independence of the reaction of any pressure change. If such were the case, a lowering of the mean free path 180 times, which corresponds to a pressure change from 5 to 900 mm., should affect the reaction. The proportionality of the rise in quantum yield and the increased velocity also indicate that every absorbing molecule reacts.

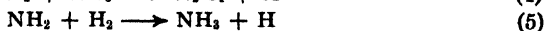
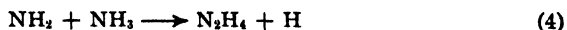
From these considerations we have been led to suggest a mechanism which, while not entirely satisfactory, is in better accord with all the data available. After the absorption



every activated molecule undergoes an initial reaction. This may occur in either of two ways



If (3) were the process occurring, the amino group would then react either with an ammonia molecule or a hydrogen molecule, if any were present.



While exact thermal data are of course unavailable on Reactions (4) and (5), it is quite probable that they will go.¹⁵

It is to be observed that these reactions would result in little or no pressure change and so would not be measured in the quantum yields. The decomposition of hydrazine would determine the measured reaction. This might occur photochemically, thermally or both. The sudden drop in yield to 10 $h\nu$ /mol. when a narrower band of spectrum is used points to the inability of hydrazine to absorb these wave lengths. The deficiency of the yield at low temperatures would be due to the reversal of Reaction (4). The increased yield and velocity with rising temperature might be due to a faster decomposition of the hydrazine preventing this reversal, or to a more rapid recombination of hydrogen atoms, which would be effective in the same way. In connection with the latter, it is of interest that the value of the temperature coefficient corresponds to the increase in collision frequency. A more detailed treatment of this phase of the reaction is not feasible, however, with the evidence on hand.

It may be pointed out that Reaction (5) and the reversal of (4) would account for both the slowing up of the reaction with time and the large retarding effect of admixed hydrogen.

There are several difficulties with this mechanism. It does not account for the fact observed by Warburg that hydrogen does not affect the reaction at low temperatures, nor is the maximum quantum yield of two in accord with Kuhn's value of three for high temperatures. However, there is no alternative explanation which fits the sum total of the data as well as this one, which is certainly a step in the right direction.

An attempt was made to show the presence of hydrazine after illumination of ammonia by the hydrogen discharge tube already described. It was hoped that absorption bands would appear which would differ from those of ammonia. We were, however, unable to detect any change in the absorption spectrum of ammonia after illumination for fifteen minutes.

In the course of this work it was observed that instead of a single band at 2260 Å., as reported by Leifson,¹⁶ there were two distinct bands. Measurements showed them to extend from 2266–2262 Å. and from 2262–2259 Å. (Fig. 5). The next band toward lower wave lengths, which marks the beginning of the series of bands described by Leifson as extending down to 1500 Å., begins at 2254 Å. It was not possible to distinguish the exact limits of the interval separating the two bands and so the center was recorded. A densitometer curve of one of the plates is given in Fig. 6.

¹⁵ See Taylor, *Proc. Roy. Soc. (London)*, 113A, 85 (1926)

¹⁶ Leifson, *Astrophys. J.*, 63, 73 (1926).

Ethylene.—The resulting products from the decomposition of ethylene (H_2 , 88%; C_2H_2 , etc., 12%) bear out in general the conclusions already advanced concerning the decomposition of this substance. The appearance of hydrocarbons in the gas phase after cooling in liquid air, however, seems to indicate that there are reactions occurring other than a pure



Fig. 5.

dehydrogenation. There is a possible explanation of this in that any ethane formed, and also ethylene, would exert a constant, small vapor pressure at liquid-air temperatures and be burned by the copper oxide. In support of this is the fact that we were never able to burn these products to less than 0.3 mm. pressure, even with liquid air surrounding the trap.

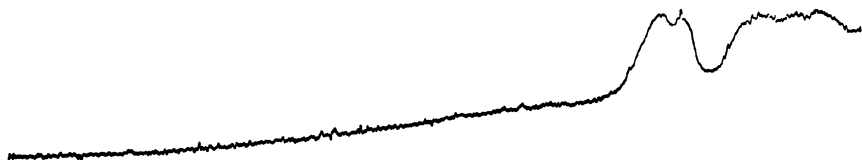
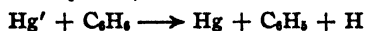


Fig. 6.

Ethyl and Methyl Alcohols.—The decomposition of the alcohols takes place through the intermediate formation of the aldehydes. Tests for acetaldehyde and formaldehyde were given by the products condensed in the liquid-air traps. While ethyl alcohol was apparently more easily decomposed, the ratio of the photosensitized to photochemical decomposition was greater in the case of methyl alcohol.

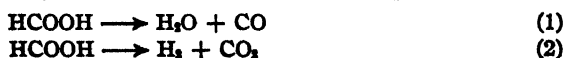
Hexane.—Hexane showed the largest divergence between the photosensitized and photochemical rates. Here again the process seems to be one of dehydrogenation, with only a small amount of hydrocarbon appearing in the gas phase.

Benzene.—While the pressure of the gaseous products is here the lowest obtained (0.3 mm.), it does not necessarily hold that this is due to the inefficiency of the excited mercury atoms in decomposing this substance. A heavy, tarry residue is deposited on the reaction vessel and a strong odor of diphenyl is present. If the reaction brought about by the mercury is one of dehydrogenation, as it is in most of the cases, it is evident that a hydrogen atom must be split off, since each carbon has but one hydrogen attached.



The probability of two hydrogen atoms recombining before reacting with a benzene molecule is extremely small, which would account for the small amount of gas formed. The appearance of such large proportions of hydrocarbons (40%) can be accounted for only upon the assumption that, in addition to dehydrogenation, a mercury atom, by transferring the energy, can also bring about a complete rupture of the benzene ring.

Formic Acid.—The decomposition of formic acid can take place in two ways



Ramsperger and Porter¹⁷ have shown that on illumination with a hot arc 64% of the decomposition occurs according to (1). Our results show, with the excited mercury, 76%. This is of much interest since it proves that the same quantum of energy transferred by a mercury atom can decompose a molecule in two ways. This cannot be due to the photochemical reaction, since the latter is only 0.25% of the total reaction, and we get 24% going according to (2). There are two means whereby the mercury atom may accomplish this "two type" decomposition. It may involve a steric effect of the collision of the mercury atoms and the molecule, or it may be that the energy, once transferred, is distributed in different ways among the vibrational degrees of freedom and thus brings about two kinds of reactions. Some evidence as to which is the case is being sought in this Laboratory at the present time by illumination of formic acid with monochromatic light. If both types of reaction still occur, it is purely a matter of the distribution.

Acetone.—This substance is so photosensitive itself that only a twofold increase in velocity was observed. In the photosensitized reaction, however, the product condensing in the liquid-air trap had a yellow color which was absent in the purely photochemical reaction.

Ethylamine.—This is another example of the type of reaction exhibited by ammonia. An intermediate compound is formed, giving a large excess of hydrogen in both types of decomposition.

Summary

1. A new type of cooled mercury arc for use in mercury sensitized and general photochemical reactions has been described.
2. By increasing the energy input into a high-pressure hydrogen discharge a continuous ultraviolet spectrum to 1900 Å. can be obtained and recorded with short exposure.
3. Ethylene condenses under the influence of excited mercury atoms with an initial rise in pressure. This does not occur by the action of light alone. The initial rise is due to the formation of acetylene and hydrogen and is regulated by the diffusion of these products from the zone of the excited mercury atoms.
4. Acetylene is polymerized by both excited mercury atoms and by ultraviolet light. Acetylene cannot be hydrogenated by hydrogen activated by excited mercury.
5. Hydrogen peroxide, formed in the mercury photosensitized reaction between hydrogen and oxygen, can be obtained as the sole product under certain conditions.
6. Water, ammonia, ethylene, ethyl and methyl alcohols, benzene, hexane, formic acid, acetone and ethylamine are decomposed by excited mercury atoms.
7. The decomposition products of ammonia show an excess of hydrogen over stoichiometric proportions. A mechanism is advanced for the photochemical decomposition of ammonia based on this and other data. The absorption spectrum of ammonia has been studied.

¹⁷ Ramsperger and Porter, *THIS JOURNAL*, **48**, 1267 (1926).

8. Excited mercury atoms can decompose a formic acid molecule in two ways.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]
THE MAGNETIC SUSCEPTIBILITIES OF THE POSITIVE IONS OF VANADIUM

BY SIMON FREED

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The view of Lewis¹ that the magnetic moments associated with the electrons in atoms or molecules usually neutralize each other in pairs has been confirmed by magnetochemical observations and by the analyses of spectra.^{2,3,4} No atom or molecule containing an odd number of electrons is known to be diamagnetic.⁵ However, there are numerous examples of paramagnetic atoms and molecules which contain an even number of electrons. Aside from the oxygen molecule, all such cases are to be found toward the centers of the long periods of the Periodic Table. The ions of vanadium investigated here occur in the first of these periods.

Hund's⁶ remarkable success in arriving at the magnetic moments of the ions of the rare earths in solution, from spectroscopic information alone, has raised the hope that the electronic configurations of all ions in solution might be determined and that an insight into their behavior might be obtained from spectroscopic data and the quantum theory.

A word should be said upon the relation of spectra to magnetic moments. In the evaluation of spectral lines it has been found possible to assign definite quantities of angular momentum to the electron (or electrons) in each orbit. The angular momentum of an electron is intimately related to its magnetic moment. More recently, the electron itself is pictured as spinning and the ratio in Bohr units of its magnetic moment to its mechanical moment is two. In general, the ratio between the magnetic moment and the resultant mechanical moment is some simple rational fraction, a value deduced in each case from observations on the anomalous Zeeman effect.

Hund⁶ supposed that the regularities found in the spectra of other ions existed in the spectra of the rare earths. This assumption led him to

¹ Lewis, *THIS JOURNAL*, **38**, 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York City, 1923.

² Lewis, *Chem. Reviews*, **1**, 231 (1925).

³ Kemble, "Molecular Spectra in Gases," p. 304, *Bul. Nat. Res. Council*, **1926**, No. 57.

⁴ Sommerfeld, "Three Lectures in Atomic Physics," Methuen and Co., London 1926, Lecture III.

⁵ Taylor and Lewis, *Proc. Nat. Acad. Sci.*, **11**, 456 (1925).

⁶ Hund, *Z. Physik*, **33**, 855 (1926).

assign in an unbroken sequence the character of the basic term of each ion, that is, the net angular momentum of the ion in its most stable state. Then, by applying the rules holding universally in the anomalous Zeeman effect, he calculated the magnetic moment of the ion in the gas. These values were almost identical with the values obtained from the crystals and from solution.⁷

Laporte and Sommerfeld⁸ have extended Hund's ideas to apply to the series of the elements from scandium to copper. Their predictions demand a knowledge of the energy intervals between the multiplet levels of the basic terms of the ions. Because of the complexity of these atoms such a knowledge will not be obtained for a considerable time. Moreover, the work to be herein described will show their conclusions to be highly improbable.

Magnetic Measurements in Solution

Magnetic susceptibilities of many substances have been measured but most of the results obtained have been vitiated by the magnetic impurities in the samples investigated. Recently some accurate work has been done.

Among the measurements that deserve the highest confidence are those of water and those of nickel chloride solutions—both of which were taken as standards for this investigation. The value adopted for the gram susceptibility of water at 20° was -0.720×10^{-6} , based upon the elaborate determination of Piccard and Devaud,⁹ who obtained -0.7199×10^{-6} with a probable relative error of 0.01%.¹⁰

The value 4383×10^{-6} was used for the molal susceptibility of NiCl_2 at 20.0°. This is the value obtained by Brant¹⁰ and was found to be constant over a 3000-fold change in concentration with a claimed accuracy of 0.1% in the portion of the range used here as standard.¹¹

Principle of Method

The method used was an adaptation of the Gouy method which depends upon having a cylinder with one end in a uniform field and the other end in a field of negligible intensity. The force on the cylinder depends upon the difference between the susceptibility per unit volume of the medium surrounding the cylinder and the susceptibility of the cylinder.

⁷ Decker, *Ann. Physik*, 79, 324 (1926).

⁸ Laporte and Sommerfeld, *Z. Physik*, 40, 333 (1926).

⁹ Piccard and Devaud, *Arch. sci. phys. Nat.*, 5, 2 (1920).

¹⁰ Brant (*Phys. Rev.*, 17, 678 (1921)), whose values for nickel chloride were used here, by assuming the above value for water, checked the susceptibility of air obtained by Soné (*Phil. Mag.*, March, 1920, p. 345) within 0.1%. Seves' (*Ann. chim. phys.*, [8] 27, 189, 425 (1912)) value for water was -0.720×10^{-6} . Weiss and Piccard (*Compt. rend.*, 155, 1234 (1912)) obtained -0.7193×10^{-6} .

¹¹ The results obtained by Miss Brant checked well with those of Cabrera, Moles and Guzman (*Arch. Sci. Phys. Nat.*, 37, 325 (1914)) and those of Weiss and Bruins (*Proc. Acad. Sci. Amsterdam*, 18, 346 (1915)), whose accuracy was probably within 1%.

A null method utilizing this fact was suggested by Professor G. N. Lewis. Cylinders of various susceptibilities were balanced horizontally against liquids of known susceptibility. These cylinders were then used to determine the unknown susceptibilities of the solutions under investigation.

Various devices were tried out to realize the advantages of such a null method. In the earlier experimentation on the method the writer had the benefit of the coöperation of Dr. S. S. Shaffer.

Apparatus

EW is a Pyrex glass tube, 11 mm. in diameter at E and about 1 mm. at W. It is filled with nickel chloride solution and sealed at O where it is fastened by means of a strip of compressed paper and screws to a brass rod Y grooved to give the rod lightness and rigidity. The latter is fastened above to an angled brass frame which has an agate knife-edge H. The knife-edge rests on a polished horizontal agate plate fastened to a heavy brass bar. The latter is screwed to 4" X 4" uprights which are in turn bolted to the iron base of a powerful electromagnet. ZZ are nuts with which the center of gravity of the swinging system can be adjusted for its optimum sensitivity.

The "bath" in which the tube E is immersed is shown with its top view at A. The tube N about 12 mm. in diameter permits the circulation and mixing of the solution, which is done by a stirrer (not drawn) in the extreme right end of the bath, above the tube N. The portion EK' fits between the pole pieces of the magnet. The latter is of the Weiss type. It produces a field of about 19,000 gauss in a pole gap 2 cm. in diameter and 2 cm. long.

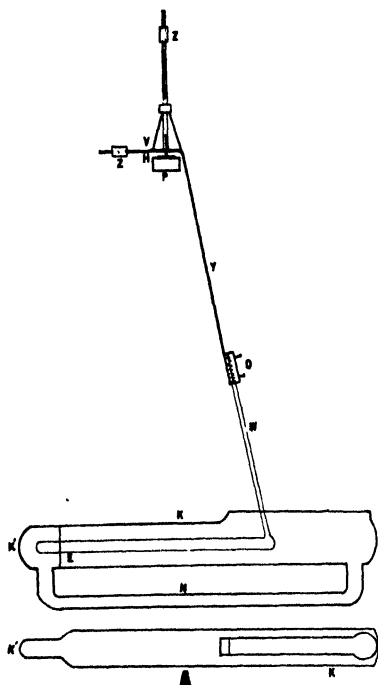


Fig. 1.

Materials

All the vanadium salts used were made from the same sample of hydrated vanadium pentoxide. The latter and the nickel chloride used for standardization were analyzed

by the systematic analytical procedure of Noyes and Bray¹² and of Noyes, Bray and Spear¹³ for the common and rarer elements. The sensitive color reactions for Fe, Co, Mn, Cr, Ni, Mo and Ti were taken advantage of and comparison was made with color standards in water or ether or, in the case of vanadium, in the vanadium solutions themselves, so as to eliminate any influence of the dissolved substances upon the sensitivity of the tests.

Sodium chloride was tested only for iron before its diamagnetic measurements. Perchloric acid and sulfuric acid were analyzed only for the commoner substances.

¹² Noyes and Bray, *THIS JOURNAL*, 29, 137 (1907).

¹³ Noyes, Bray and Spear, *ibid.*, 30, 481 (1908).

The hydrated vanadium pentoxide was found to contain 0.35 mole of sodium in the form of vanadate and 0.015 mole of acetate for every mole of vanadium in the sample. The amounts of potassium permanganate used to oxidize the same sample of vanadium pentoxide twice in succession after it had been reduced with sulfur dioxide were practically identical.

Because of its diamagnetism the effect of the acetate upon the results was neglected.

Analysis

The quantitative analysis of vanadium in its different valence states was made by titrating with standard potassium permanganate solution, which oxidized all of the vanadium to the quinivalent condition. Then through the resulting solution sulfur dioxide gas from a cylinder was passed which reduced all of the vanadium to the quadrivalent state. By reoxidizing this quadrivalent vanadium with the standard potassium permanganate solution the total vanadium was found. These two titrations were sufficient to determine the concentrations of vanadium of two different valences. It was assumed that not more than two can coexist in the solution because of their extreme reactivity.

Rutter¹⁴ has reported the rapidity with which these ions interact.

The reduction of vanadium by sulfur dioxide for its quantitative determination was highly recommended by Treadwell and Hall,¹⁵ Hillebrand¹⁶ and Lundell and Knowles,¹⁷ whose precautions were strictly followed.

The sulfate present in solutions containing quadrivalent vanadium (VO^{++}) was found to be quantitatively precipitated by barium chloride solution. In the analyses for sulfate, the trivalent and bivalent vanadium solutions were left exposed to the air to be oxidized to the quadrivalent state before the sulfate analyses were made.

Mode of Operation and Standardization of Tubes

Five tubes such as EW were filled with different concentrations of nickel chloride solution and sealed at O. Each tube was standardized by filling the bath in which the tube was immersed with pure nickel chloride solution and by adjusting its concentration until the tube would swing neither in one direction nor in the other when the magnetic field was on. After the balance had been reached in a field of about 19,000 gauss, samples were taken out of the bath and analyzed. The density of the solution was taken and also its temperature.

In the case of unstable substances, calibrated pipets were "washed" with carbon dioxide until they touched the bath. The pipet filled with the solution was allowed to drain to the mark and then into a flask filled with carbon dioxide and containing sulfuric acid solution and a known amount of potassium permanganate. As the pipet was being drained into the flask, a stream of carbon dioxide was passed just over the top of the pipet.

During the standardization of the tubes the effect of one drop of water in 175 cc. of solution in the bath could be detected when the more concentrated solutions (about 0.20 molal nickel chloride) were being measured.

In the following table are the concentrations of nickel chloride which balanced each tube and the corresponding susceptibilities per unit volume. These values were

¹⁴ Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

¹⁵ Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York City, 4th edit., Vol. II, p. 636.

¹⁶ Hillebrand, "Analysis of Silicates," United States Geological Survey Bulletin, No. 78.

¹⁷ Lundell and Knowles, *THIS JOURNAL*, **43**, 1560 (1921).

computed by taking -0.720×10^{-6} as the susceptibility of a gram of water and 4383×10^{-6} as the susceptibility of a mole of nickel chloride at 20° .

A variation of 3° had no measurable effect upon the concentration necessary to balance each tube.

Independent magnetic measurements of the same tube gave identical results as far as analyses could disclose, that is, within 0.2%.

TABLE I
STANDARDIZATION OF TUBES

Tube	Molal concn., NiCl_2	Density	G. H_2O cc. soln.	$\chi_{\text{cc}}^{20^\circ} \times 10^6$
1	0.2766	1.0310	0.9951	+0.4958
2	.2191	1.0242	.9958	+ .2433
3	.1618	1.0176	.9966	- .0083
4	.1119	1.0115	.9970	- .2275
5	.07927	1.0076	.9973	- .3707

^a $\chi_{\text{cc}}^{20^\circ}$ is the susceptibility per cc. at 20° .

Diamagnetic Measurements

All of the constituents of the solution have associated with them definite amounts of diamagnetism. The diamagnetism of the magnetic ions will be discussed later. The diamagnetism of all the other ions was determined by the Gouy method described by Shaffer and Taylor.¹⁸

Wiedemann's law of the additivity of ionic susceptibilities was used in these evaluations as well as in the paramagnetic ones. To determine the susceptibilities of single ions the diamagnetism of one of the ions had to be known from some other source. The value -20×10^{-6} was taken for the atomic susceptibility of Cl^- . This value is in accord with the theoretical considerations on diamagnetism of Joos,¹⁹ who obtained -19.5×10^{-6} , and the experimental work of Pascal,²⁰ who obtained -20×10^{-6} from his magnetic work on organic compounds and on chlorine gas.

The following table gives the diamagnetic susceptibilities. They are the mean of a number of measurements and are good to about 5%.

TABLE II
DIAMAGNETIC MEASUREMENTS

Subs.	Times measured	Molality	Density	G. H_2O cc. soln.	$\chi_{\text{cc. soln.}}^{20^\circ}$	$\chi_{\text{moles solute}}^{20^\circ}$
NaClO_4	4	5.47	1.3866	0.670	-0.740	-41×10^{-6}
NaCl	5	4.63	1.1730	.901	- .800	-32.6×10^{-6}
HClO_4	3	9.04	1.522	.613	- .720	-31×10^{-6}
H_2SO_4	2	0.993	1.0580	.961	- .732	-41×10^{-6}
H_2SO_4	2	17.9	1.8323	.0733	- .752	-39×10^{-6}

¹⁸ Shaffer and Taylor, *THIS JOURNAL*, **48**, 843 (1926).

¹⁹ Joos, *Z. Physik*, **19**, 347 (1923).

²⁰ (a) Pascal, *Ann. chim. phys.*, [8] **16**, 520 (1909); (b) **19**, 1 (1910); (c) **25**, (1912); (d) **29**, 218 (1913).

From Table II the following values were adopted, $\chi_{\text{ClO}_4^-}^{20^\circ} = -28 \times 10^{-6}$; $\chi_{\text{SO}_4^{--}} = -37 \times 10^{-6}$; $\chi_{\text{Na}^+} = -12 \times 10^{-6}$.

Quadrivalent Vanadium Ion

The basic idea which was constantly kept in mind was to introduce a minimum of foreign matter into the solutions so as to keep the corrections as small as possible. All solutions were prepared at room temperature or below to avoid hydrolysis and other complications that might accompany higher temperatures. It appears that if cobalt chloride solution be warmed its molal susceptibility thereafter varies with the concentration but it remains constant if not warmed.

To minimize the danger of the formation of complex ions Professor G. N. Lewis suggested that the perchlorates should be used whenever feasible.

Preparation of Solution.— $\text{VO}(\text{ClO}_4)_2$ solution was prepared by suspending the hydrated vanadium pentoxide in a solution of perchloric acid containing a known amount of the acid. Hydrogen sulfide gas made by dilute sulfuric acid reacting with iron sulfide was washed in water and then conducted slowly into the solution. The liberated sulfur was filtered off through a Jena porous-glass filter and then the excess of hydrogen sulfide was pumped off at room temperature with a Nelson vacuum pump. Some of the blue $\text{VO}(\text{ClO}_4)_2$ solution was taken and carbon dioxide was passed through it and then into very dilute potassium permanganate solution for five minutes without decolorizing the pink solution.

As some authors claim that vanadium pentoxide reduced with hydrogen sulfide requires a little more potassium permanganate for its reoxidation than vanadium pentoxide reduced with sulfur dioxide, the $\text{VO}(\text{ClO}_4)_2$ solution freed from hydrogen sulfide was shaken with solid vanadium pentoxide and then filtered. Upon titrating the resulting solution with potassium permanganate solution, reducing with sulfur dioxide and titrating again, about 0.5% of quinquivalent vanadium was found in the solution. The amount of the latter increased to 0.9–1.0% by the time the last of the magnetic measurements on quadrivalent vanadium were finished.

The effect of so small an amount of diamagnetic²¹ substance was negligible.

The solution was diluted to a definite volume before any had been removed for detecting unevaporated hydrogen sulfide in order to fix the concentration of ClO_4^- . The concentration of total vanadium was determined in this volume and since the total number of moles of perchloric acid was known, a definite ratio of the concentrations of total vanadium to total perchlorate was fixed. This ratio remained unaltered

TABLE III
SUSCEPTIBILITY OF QUADRIVALENT VANADIUM ION

	Molal concn., VO^{++}	Concn. $\text{Na}^+ \times$ VO^{++}	Concn. total $\text{ClO}_4 \times \text{VO}^{++}$	Concn. $\text{H}^+ \times$ VO^{++}	G. H_2O cc. soln.	Density of soln.	$\chi \times 10^6$, cc. soln.	$\chi_{20^\circ} \times 10^6$ Moles VO^{++}
I	0.9555	0.35	2.57	0.214	0.900	1.2152	+0.4958	1275
II	.7553	.35	2.57	.214	.920	1.1695	+ .2433	1277
III	.5585	.35	2.57	.214	.941	1.1255	— .0083	1276
IV	.3858	.35	2.57	.214	.957	1.0855	— .2275	1274
	.2739	.35	2.57	.214	.971	1.0618	— .3707	1274

²¹ Ref. 20 a, p. 565.

throughout the various magnetic runs as it obviated the repeated analyses for ClO_4^- . The concentration of total vanadium in any solution automatically gave the concentration of total perchlorate.

Magnetic Measurements.—The data obtained on quadrivalent vanadium ion are given in the preceding table.

Trivalent Vanadium Ion

Preparation of Solution.—Rutter's¹⁴ suggestion that platinized platinum serve as the cathode in the electrolytic reduction of quadrivalent vanadium to trivalent vanadium was adopted.

As perchlorate ion is reduced by trivalent vanadium ion, the sulfate was used.

Vanadyl sulfate, prepared as described in the preceding section, was reduced in an electrolytic cell of about 200 cc. capacity. The latter consisted of a cathode of platinized platinum and of an anode of platinum wire. The latter was dipped into a dilute sulfuric acid solution in an aluminum thimble. Carbon dioxide at least 99% pure, which was passed through potassium permanganate solution and then through distilled water, was bubbled through the electrolyte.

The color changed gradually from a bright blue to a greenish-brown. This brown solution was filtered in an atmosphere of carbon dioxide through a Jena porous-glass filter.

Magnetic Measurements.—The data of the magnetic measurements are given in the following table.

TABLE IV
SUSCEPTIBILITY OF TRIVALENT VANADIUM ION
Brown variety, assuming trivalent present only as VO^{2+} ^a

	Molal concn., VO^{2+}	Concn. VO^{2+}	Concn. V^{2+}	Concn. Na^+	Concn. SO_4^{--}	G. H_2O cc. soln.	Density	$\chi \times 10^6$, cc. soln.	$\chi_{300} \times 10^6$, VO^{2+}
I	0.3216	0.1116	0.1520	0.614	0.985	1.0765	+0.4958	3382
II	.2559	.080111220	.476	.987	1.0580	+ .2433	3405
III	.1942	...	0.0086	.0710	.284	.991	1.0337	— .0083	3415
IV	.1289	.05340638	.259	.992	1.0308	— .2275	3331

Green variety, assuming trivalent present only as V^{3+} ^b

	Molal concn. V^{3+}	Concn. VO^{2+}	Concn. H^+	Concn. Na^+	Concn. SO_4^{--}	G. H_2O cc. soln.	Density	$\chi \times 10^6$, cc. soln.	$\chi_{300} \times 10^6$, V^{3+}
V	0.2160	0.0163	0.33	0.0813	0.544	0.988	1.0538	— 0.0083	3261
VI	.1528	.0081	.21	.0563	.370	.991	1.0366	— .2275	3208
VII	.1076	.0073	.15	.0402	.264	.994	1.0261	— .3707	3216

^a If an attempt were made to calculate the susceptibility on the basis of V^{3+} , that is, disregarding the contradiction of inequality of positive and negative constituents, all values of magnetic moments would be about 0.3% higher.

^b The deficiency in sulfate to form just a neutral solution if V^{3+} were assumed is: I, 0.053 molal; II, 0.046 molal; III, 0.050 molal; IV, 0.019 molal. (The greater the deficiency, the less the H^+ concentration.)

A few remarks are necessary here. The brown solution of the preceding paragraph was measured magnetically and then analyzed. It was found to be a mixture of trivalent and quadrivalent vanadium; but the amount of sulfate present, known to within 1%, did not agree with the formula

V^{+++} for trivalent vanadium but accorded well with the assumption that the trivalent vanadium was present chiefly as VO^+ .

In the literature trivalent vanadium is described as green and its formula is usually given as V^{+++} . Indeed, the crystals of $V_2(SO_4)_3$ have been isolated out of a solution containing six-molal sulfuric acid.

A little more sulfuric acid was added in the next electrolytic reduction and the color of the final product was pure green as was expected.

The first four solutions tabulated were prepared independently; the green solutions were dilutions from one electrolytic reduction. An attempt to make the electrolyte even less acid than in I, II and III resulted in the gradual settling out of a greenish-gray precipitate.

The brown variety oxidized in the bath rapidly, although there was a heavy stream of carbon dioxide constantly entering the paraffin pocket.

In II an innovation was introduced. Xylene was put over the solution in the bath until it formed a layer 5 mm. thick. Moreover, the stream of carbon dioxide was not interrupted. Under these conditions, the deflection of the balance was the same before and after two minutes of rapid stirring, that is, the oxidation was sufficiently slow.

It should be observed that the results with xylene are the same as the one without xylene.

The Use of Xylene

Twenty cc. of xylene did not affect the color caused by one drop of 0.03 *N* potassium permanganate although the mixture was vigorously agitated. Ten cc. of xylene in contact with V^{++} for a day, as well as several cc. in contact with the trivalent for a week behaved similarly.

Benzene dissolves in water only to about 0.08% by volume. Toluic acid is given in the tables as less soluble in water than benzoic.²² Saturated aliphatic compounds are less soluble than aromatic. From the work of Conant and Cutter²³ on the action of bivalent vanadium on organic substances, it was concluded that its reduction of xylene was nil or negligible. Even if xylene were reduced, the product formed would be less soluble than xylene itself. Its diamagnetic effect could certainly be ignored, particularly as the difference in its diamagnetism from that of water would have to be considered. *Henceforth xylene was always used over the bath.*

The effect of carbon dioxide was also neglected. Its diamagnetism is quite high, -0.42×10^{-6} per gram according to Soné²⁴

The difference between this value and that of water is involved. A correction would amount to less than 0.1% in the magnetic moment.

Bivalent Vanadium

Preparation of Solution.—Bivalent vanadium was prepared from $VOSO_4$ in the same way as trivalent vanadium, except that a mercury cathode was used instead of a platinum one. The solution was surrounded with ice but in order to avoid local heating a low current density was used.

²² Hertz, *Ber.*, 31, 2671 (1898).

²³ Conant and Cutter, *THIS JOURNAL*, 48, 1016 (1926).

²⁴ Stoner, "Magnetism and Atomic Structure," Dutton and Co., New York, 1926, p. 268.

The color changed in some cases from the blue of the vanadyl to a brownish-green, then to a lavender, and in others from the blue to a deep brown with a greenish hue and then to lavender. The variation through the trivalent state depended upon the original acid concentration. The acid concentration was kept low and in every case a fine precipitate formed as the reduction passed through the trivalent state, a precipitate which did not redissolve.

The first attempt to prepare the bivalent vanadium resulted in a solution containing some of this precipitate and it catalyzed the decomposition of water to such an extent as to decompose 23 to cc. out of 150 cc. in fifteen minutes.

The tube through which the carbon dioxide was bubbled into the cell was later used to siphon the solution through a porous-glass filter into a filter flask connected to a vacuum pump. The filter was in a Gooch funnel which reached to the bottom of the filter flask, in which there were about 10 cc. of xylene. The system was filled with carbon dioxide before evacuation began. In its passage from the electrolytic cell, which was constantly in operation and evolving hydrogen, to the filter flask the bivalent vanadium did not come in contact with the atmosphere.

The concentration of the acid was reduced and a solution of bivalent vanadium was finally prepared which could be handled with comparative ease.

Magnetic Measurements.—The following table (V) gives the results. As will be observed, the bivalent vanadium was contaminated with a considerable amount of trivalent vanadium. If the trivalent had been assumed to be of the form V^{+++} , there would still have been a surplus of SO_4 to account for the H^+ tabulated. It was then obvious that the trivalent vanadium present was of the "green variety" considered under "Trivalent Vanadium."

For purposes of correction, the average of the three green solutions of trivalent vanadium was used, that is, 3228×10^{-6} as the molal susceptibility of V^{+++} at 20° .

TABLE V
SUSCEPTIBILITY OF BIVALENT VANADIUM ION

	ANALYSED concn., V^{++}	Concn. V^{+++}	Concn. H^+	Concn. Na^+	Concn. SO_4^{--}	Density	G. H_2O cc. soln.	$\chi \times 10^6$, cc. soln.	$\chi_{390} \times 10^6$, molal
I	0.1890	0.01616	0.066	0.072	0.281	1.0347	0.996	+0.4958	6204
II	.1381	.0315	.13	.059	.279	1.0310	.994	+.2433	6290
III	.1018	.0247	.080	.044	.208	1.0225	.995	-.0083	6255
IV	.07217	.01651	.074	.031	.148	1.0158	.996	-.2275	6129
V	.04614	.02065	.044	.0234	.111	1.0116	.997	-.3707	6175
VI*	.1833	.0218	.096	.072	.310	1.0364	.995	+.4958	6297

* Preliminary run included to show that the peculiar increase in grams H_2O per cc. of solution was probably real. In the preliminary run, the solution was heated to evaporate the excess of sulfur dioxide gas in the reduced vanadium pentoxide solution. It was then cooled in ice and electrolyzed. The regular solutions were never heated.

In the calculations, the presence of carbon dioxide in the solution was ignored, as was done previously.

Aside from the experiments whose results have been tabulated, only one other complete magnetic run on the vanadium ions was made. This was rejected because of a poor check in the analyses.

Discussion of Errors

The cumulative effect upon the susceptibility of the quadrivalent vanadium ion of all the substances ignored in the calculations, such as dissolved air, carbon dioxide, etc., is probably not more than 0.3% (or 0.15% in the magnetic moment). The effect of each substance is in general to reduce the apparent susceptibility because of the very high diamagnetic susceptibility of one gram of water.²⁵

The errors in the analysis of quadrivalent vanadium are probably not greater than 0.2%, those of trivalent vanadium not greater than about 0.5% and those of the bivalent ion not greater than about 0.8%. In the two latter cases, the reflection of these analytical errors upon the susceptibilities is not as serious as it appears to be. The concentration of total vanadium even here was determined within about 0.3% and a decrease in the bivalent vanadium (if that be the ion under consideration) due to an analytical error would increase the trivalent ion impurity and so the resultant error would involve the differences in the susceptibilities of these two constituents and not one only.

More serious sources of error are the diamagnetic corrections and the correction for V^{+++} in V^{++} solutions.

The uncertainty in the value of e/m is of vital importance when the magnetic moments are considered, especially in the case of quadrivalent vanadium ion.

Discussion of Results

Change of susceptibility with change in acid concentration is common. It is usually attributed to the formation of complex ions. The latter probably result from the pairing of unbalanced electrons. It is not surprising then that the susceptibility of the trivalent ions should decrease with increasing H^+ concentration. The variation in susceptibility of the bivalent vanadium ions might be due almost entirely to the accompanying trivalent vanadium ions. As previously mentioned, it was the constant aim to have a minimum of acid present.

Langevin²⁶ arrived at the following formula connecting the susceptibility of a paramagnetic gas with its magnetic moment for ordinary field strengths and at room temperature

$$\chi T = \frac{M^2}{R} \overline{\cos^2 \Theta}$$

where M is the magnetic moment of a mole of the gas, R is the gas constant, T is the absolute temperature and $\overline{\cos^2 \Theta}$ is the mean of the square

²⁵ The content in water was determined by the difference between the calculated weight of the dissolved substances in 1 cc. listed in the tables and the specific gravity of the solutions.

²⁶ Langevin, *Ann. chim. phys.*, [8] 5, 70 (1905).

of the cosines of the angle which the axis of the electronic orbit makes with the direction of the magnetic field.

The magnetic moment considered above applies only to the paramagnetism of the gas and not to the diamagnetism induced by the field, which reacts upon the susceptibility actually measured. Corrections for this diamagnetism must be estimated. Its amount is small and the error introduced in the estimation is not serious. Thus, potassium ion has a molal susceptibility of -15×10^{-6} , whereas calcium being a bivalent ion²⁷ has a smaller susceptibility, in fact -6×10^{-6} . VO^{++} because of its oxygen content is probably a little more diamagnetic than the latter.²⁸ As a rough estimate -13×10^{-6} per mole was taken. In the same way, -20×10^{-6} was taken as the molal diamagnetic susceptibility for VO^+ . That of V^{+++} and V^{++} was neglected. If the VO^{++} had been considered to have zero for its diamagnetic susceptibility, the magnetic moments tabulated would have been lowered by 0.5%.

One-half of one per cent. is about the uncertainty in our knowledge of the exact value of e/m . The value of the latter as given by Sommerfeld is employed, that is, 1.769×10^7 . Consequently, the Bohr unit of magnetic moment

$$\frac{1}{4\pi} N h \frac{e}{m} = 5584 \text{ gauss cm. per mole}$$

From this value and the Langevin equation as modified by Sommerfeld's²⁹ application of the quantum theory, the following table was calculated.

According to the quantum theory only discrete orientations of the magnetic moments with respect to the field are permissible. If the lowest term of the ion is an S term, the orientations depend only upon the resultant mechanical moment of the ion.³⁰

TABLE VI		
Units of angular momentum	Bohr magnetic units	Average squared cosines
$1/2$	1	1
$2/2$	2	$2/3$
$3/2$	3	$6/5$

For all S terms, the ratio of the magnetic moment to the mechanical moment is exactly two. For basic levels other than S the ratio is in general non-integral. Using the $\overline{\cos^2\Theta}$ listed in each table, the following values were obtained for the magnetic moments.

²⁷ Ref. 24, p. 271.

²⁸ Pascal, ref. 20, found that O in organic compounds has the atomic susceptibility of -4.6×10^{-6} .

²⁹ Sommerfeld, *Z. Physik*, 19, 221 (1923).

³⁰ Sommerfeld, "Atombau und Spektrallinien," Vieweg and Son, Braunschweig, 1922, 4th ed., p. 639.

TABLE VII
MAGNETIC MOMENTS OF THE POSITIVE IONS OF VANADIUM
Quadrivalent Bohr Magnetons— $\overline{\cos^2\Theta} = 1$

Run no. ^a	I	II	III	IV	V
Moments	1.004	1.004	1.004	1.003	1.003

Trivalent— $\overline{\cos^2\Theta} = \frac{2}{3}$
Brown—low acid concentration

Run no.	I	II	III	IV
Moments	1.997	2.004	2.007	1.982

Green—higher acid concentration

Run no.	V	VI	VII
Moments	1.956	1.939	1.942

Bivalent— $\overline{\cos^2\Theta} = \frac{5}{9}$

Run no.	I	II	III	IV	V	Preliminary
Moments	2.954	2.975	2.966	2.936	2.947	2.976

^a Refers to tables of susceptibilities.

From the measurements of Cabrera³¹ it appears that Cr^{+++} has 3 (within 1%) and Cr^{++} has 4 (within 2%) Bohr magnetons. The generalization of Kossel³² that the atomic moments of all ions having the same number of electrons are equal has been found to hold ($\text{V}^{++} - \text{Cr}^{+++}$).

The three ions of vanadium and the two of chromium form a remarkable series of integral values,³³ values which would never be expected from the theory of Laporte and Sommerfeld.⁸ The values anticipated by them would be non-integral and, *a fortiori*, not a regular sequence of integral values.

Sommerfeld's modification of Langevin's equation is based upon the anomalous Zeeman effect, as observed on *atoms* and atomic ions. Why the application of such an equation to *molecular* ions in solution such as VO^{++} and VO^+ should yield integral numbers of Bohr magnetons is not at all clear.

The striking resemblance in the character of electronic levels of molecules (and molecular ions) to that of electronic levels in atoms (and atomic ions) of the same number of "valence" electrons³⁴ has caused the electronic levels of molecules to be classified as S, P, D, etc., levels in analogy to the energy levels of atoms. To determine how strict this analogy is will require much further work in band spectra.

It is highly probable that even in the case of "simple" atomic ions, such as those discussed here, the ionic individuality includes the water

³¹ Cabrera, *Anales soc. españ. fis. quim.*, 15, 199 (1917), given by Weiss, *J. phys. radium*, 5, 141 (1924).

³² Kossel, *Ann. Physik*, 49, 229 (1916).

³³ Mn^{++} and Fe^{+++} also constitute members of this series as each of them appears to have five Bohr magnetons. (Ref. 29, p. 639.)

³⁴ (a) Mulliken, *Phys. Rev.*, 26, 561 (1925). (b) Mecke, *Naturwissenschaften*, 13, 698 (1925). (c) Birge, *Nature*, 117, 300 (1926).

molecules of coordination.³⁵ The atomic ions in long periods of the Periodic Table should then be considered as of the molecular type. Presumably magnetic influences on band spectra (Zeeman effect, Paschen-Back effect) should be invoked to study them and not the anomalous Zeeman effect on atomic ions as has been done heretofore.

The writer expresses with pleasure his deep obligation to Professor G. N. Lewis for his suggestions and interest in this research. He also wishes to thank Professor W. F. Giaque for his interest in this work.

Summary

1. A new method has been developed for measuring magnetic susceptibilities.

2. The magnetic susceptibilities of the positive quadrivalent, trivalent, and bivalent ions of vanadium have been measured.

3. It appears that: (a) the quadrivalent vanadium ion has 1 integral Bohr magneton; (b) the trivalent vanadium ion has 2 integral Bohr magnetons; (c) the bivalent vanadium ion has 3 integral Bohr magnetons.

4. The above results do not agree with any current theory based upon the quantum theory and anomalous Zeeman effect. A reason for this discordance is suggested.

5. Some measurements on diamagnetic substances are included.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

STUDIES OF METHANOL CATALYSTS. I

BY HUGH STOTT TAYLOR AND GEORGE B. KISTIAKOWSKY¹

RECEIVED JULY 11, 1927

PUBLISHED OCTOBER 5, 1927

During the past few years the technique of hydrogenation catalysis in industry has undergone a revolutionary development. Until recently, hydrogenation catalysts were confined practically exclusively to a very restricted series of metals, among which platinum, nickel, copper and iron were the most important. With the industrial development of methanol synthesis, this series of catalysts has expanded fundamentally in that it has been shown that a variety of hydrogenation processes may be carried out in contact with various oxides or mixtures of the same. This extension

³⁵ Such a condition undoubtedly obtains among the ions having their outer electronic shells incompletely filled. On the other hand, among the ions of the rare earths the electrons responsible for the magnetic moments are far within the kernel and are surrounded by shells having their full complement of electrons. Under such conditions, the water molecules do not form an integral part of the ions and apparently their influence is slight, as is shown by the close agreement between the values calculated from spectroscopic studies and those observed in solution.

¹ International Research Fellow.

was an obvious development of the observations of Sabatier and succeeding workers on the activity of such oxides as dehydrogenating catalysts and on the conclusion from thermodynamic reasoning that a catalyst for a reaction in a given direction is a catalyst also for the reverse reaction.²

Thus far, the study of oxide catalysts for hydrogenation has been almost exclusively technical; little inquiry has been made into the fundamental aspects of the problem. The use of oxide catalysts for dehydrogenation processes has, on the other hand, been the object of a considerable amount of scientific study with a view to elucidating the mechanism of the catalytic action.³ As yet, however, the problem of mixed dehydrogenation and dehydration is still a matter for lively discussion. We have accordingly ventured to initiate a systematic study of oxide catalysts as hydrogenation agents, along the lines that have proved successful in this Laboratory when applied to metal catalysts. It was hoped that something could be learned, by such studies, concerning the properties of oxide catalysts in general. The reason for their superiority over metal catalysts for methanol synthesis might also be elucidated. The present paper records the results of adsorption studies with two typical methanol catalysts, zinc oxide and a mixture of zinc and chromium oxides.

The adsorption of gases by oxide catalysts has already been the subject of some little study. Benton⁴ measured the adsorptive capacity of various oxide oxidation catalysts for hydrogen and carbon monoxide. Lazier and Adkins⁵ attempted to correlate the dehydrogenation-dehydration ratio of zinc oxide with the adsorption of this oxide and other catalysts but concluded that there existed no simple relationship between the two factors. Hoover and Rideal⁶ studied the adsorptions of hydrogen and ethylene on thoria catalysts in order to learn something of the dehydrogenation-dehydration activity of thoria for ethanol. In our work, in ascertaining the adsorption of hydrogen and carbon monoxide on zinc oxide and on a mixture of zinc and chromium oxides, we were studying the capacity of a single oxide catalyst and of a well-known active methanol mixed oxide catalyst for the only two reactants of the methanol synthesis. We have also measured, in one case, the adsorption of carbon dioxide. Our results have abundantly justified the effort.

² See Rideal-Taylor, "Catalysis in Theory and Practice," 2nd edition, The Macmillan Company, New York, 1926, p. 20.

³ For a summary of this work see (a) Bancroft, Second Report of the Committee on Contact Catalysis; (b) Bischoff and Adkins, *THIS JOURNAL*, **47**, 807 (1925); (c) Taylor, Fourth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **30**, 185 (1926); (d) Taylor, Fourth National Colloid Symposium, Chemical Catalog Co., Inc., New York, 1926, p. 25.

⁴ Benton, *THIS JOURNAL*, **45**, 887, 900 (1923).

⁵ Lazier and Adkins, *J. Phys. Chem.*, **30**, 353 (1926).

⁶ Hoover and Rideal, *THIS JOURNAL*, **49**, 116 (1927).

Experimental Procedure

Apparatus.—The apparatus was essentially that used in the earlier experimental studies of adsorption on metal catalysts.⁷ A vessel containing the catalyst was connected through three-way stopcocks with a manometer, gas buret and pump system for evacuation purposes. In the present experiments the latter consisted of two mercury vapor pumps in series with a high-vacuum oil pump as fore-vacuum. The free space in the catalyst vessel was determined by a series of measurements of volume and pressure of a non-adsorbed gas, for example, nitrogen, at a controlled temperature. From the volumes of hydrogen or carbon monoxide required to fill the vessel to a given pressure at the same temperature, the extent of adsorption at this pressure could be determined.

Catalysts Employed.—Three samples of a single preparation of zinc oxide and one of a mixed zinc oxide-chromium oxide were studied. The zinc oxide was prepared by ignition at 450°, special precautions being taken to ensure that the catalyst was entirely free even from traces of alkaline or acid ions, since these may both materially alter the characteristic of the catalyst.^{3c,d} The mixed zinc oxide-chromium oxide was of the type described in patents of the Badische Company,⁸ obtained by precipitating zinc chromate from a solution of the nitrate, thoroughly washing the precipitate, drying and igniting at 450°. It contained approximately two moles of ZnO to one mole of Cr₂O₃. With both these catalysts methanol can be readily made from mixtures of hydrogen and carbon monoxide; it is well known, however, that the mixed catalyst is far superior to the single oxide.⁹ The zinc oxide samples were, respectively, 39, 39 and 32 g. The zinc oxide-chromium oxide sample weighed 25 g.

Experimental Results.—Our early experiments showed that the adsorptive capacity of a sample of the oxide was very sensitive to the cleanness of the surface. It was soon found that both zinc oxide and the mixed oxide catalyst showed no adsorption for either hydrogen or carbon monoxide even after evacuation for one hour at 300° in the high-vacuum system already described. Between 300 and 400°, however, a rapid evolution of adsorbed *water vapor* and *carbon dioxide* occurred, after which the surface of the catalyst immediately revealed pronounced adsorptive capacity for both gases.

Fig. 1 shows graphically the increase in adsorptive capacity for carbon monoxide of zinc oxide, No. 1, consequent on the increasing cleanliness of the surface, due to better evacuation. The curves 1a and 1b, etc., are corresponding runs at 100 and 0°. The initial runs with this gas,

⁷ See, for example, Pease, *THIS JOURNAL*, **45**, 1196 (1923).

⁸ Brit. pat. 227,147; U. S. pat. 1,558,559.

⁹ Patart, International Conference on Bituminous Coal, Carnegie Inst. Tech., 1926, p. 141.

after pumping off at 200°, showed identical values for nitrogen and carbon monoxide, indicating zero adsorption of the latter. The succeeding results, recorded in the order of their performance, show the progressive increase in the adsorptive capacity of the catalyst. Curves 3a and 3b were obtained after evacuation for three hours at 510°. One result with hydrogen, 4a and 4b, is also included for comparative purposes. We have found that portions of both gases are adsorbed very tenaciously and are only removed from the surface in the oxidized condition either as carbon dioxide or water vapor, partial reduction of the catalyst to a corresponding amount occurring. At first we were inclined to ascribe all of the increase in adsorptive capacity to this reduction process but we now have full evidence that even unreduced but clean surfaces of these catalysts show large adsorptive capacity for the two gases.

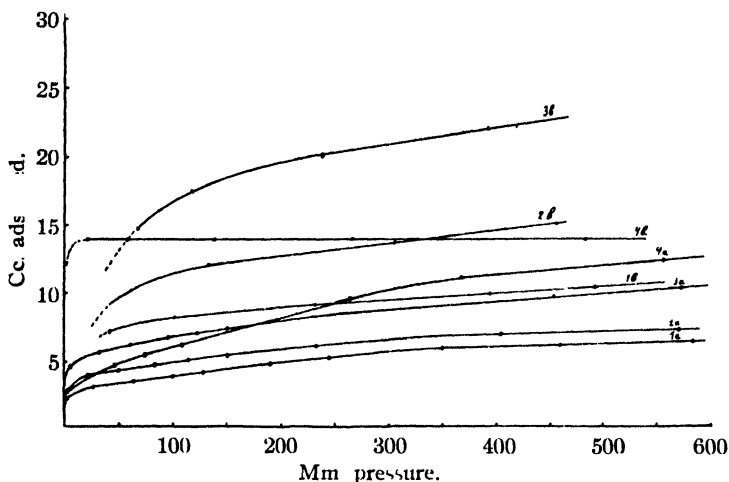


Fig 1

The reduction produces gray spots in the otherwise white zinc oxide. The reduction process is very probably an interface reaction as with copper oxide¹⁰ since the gray spots grow with increased treatment. At first we considered the possibility that the dark spots might be due to catalytic decomposition of carbon monoxide by the reaction, $2\text{CO} = \text{CO}_2 + \text{C}$, carbon being deposited in the oxide. Our experiments on zinc oxide No. 2, carried out exclusively with hydrogen, disposed of this possibility since here again the gray specks formed. The adsorption of hydrogen on this catalyst is shown in Fig. 2, Curve I, after evacuation at 450°. Since we found that a treatment at 500° with oxygen partially destroyed the adsorptive capacity (Curve II) and since oxygen was partially consumed in the process, we assumed this to be evidence in favor of adsorption

¹⁰ Pease and Taylor, *THIS JOURNAL*, 43, 2179 (1921).

by reduced zinc nuclei in the mass. An extended treatment with oxygen for 18 hours, followed by evacuation at 500° , gave a surface which subsequently showed (Curve III) high adsorption for hydrogen, thus discrediting the theory that adsorption is due *solely* to metal atoms.

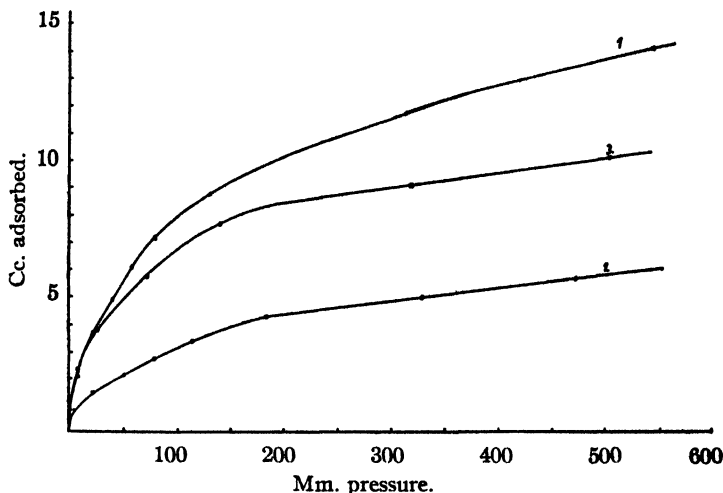


Fig. 2.

We disposed of this metal theory of adsorption by evacuating zinc oxide No. 3 thoroughly at 500° before bringing the sample into contact with any reducing gas. Curve I in Fig. 3 shows the high adsorptive capacity attained. With this catalyst we also showed the adverse effect of too

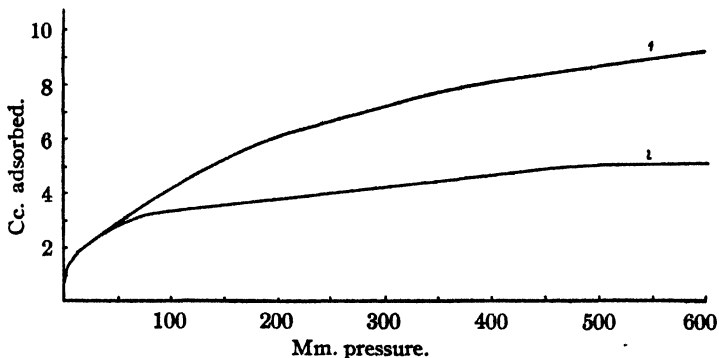


Fig. 3.

high a temperature, since Curve II shows the diminished adsorption after evacuation at 600° . This sample was very dark in color after this treatment.

In order to compare adsorptions on zinc oxide and on the mixed oxides we next made measurements on the zinc oxide-chromium oxide sample.

This adsorbed neither gas after evacuation at 200 or 300°. After half an hour of evacuation at 400°, Curve I, Fig. 4, with hydrogen was obtained. A further half hour of evacuation at 400° gave with hydrogen the results in Curve II. Curve III records results with carbon monoxide

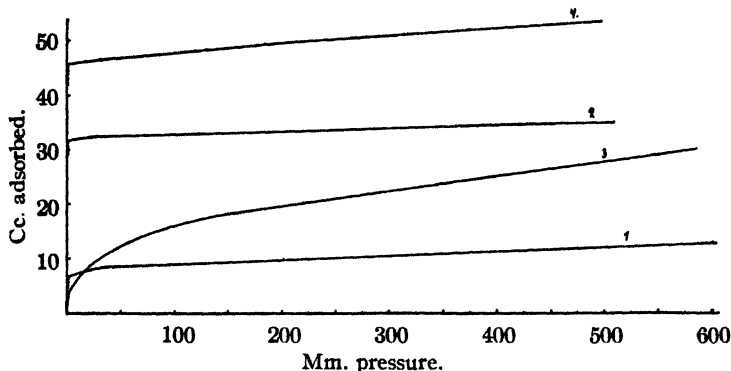


Fig. 4.

after a further half hour of evacuation at 400°. Curve IV gave hydrogen adsorption after one further evacuation for half an hour at 400°. It is very definitely established from these results that the hydrogen adsorption is more marked than that of carbon monoxide on the mixed oxide catalyst, while the reverse is true on the single zinc oxide (Fig. 1).

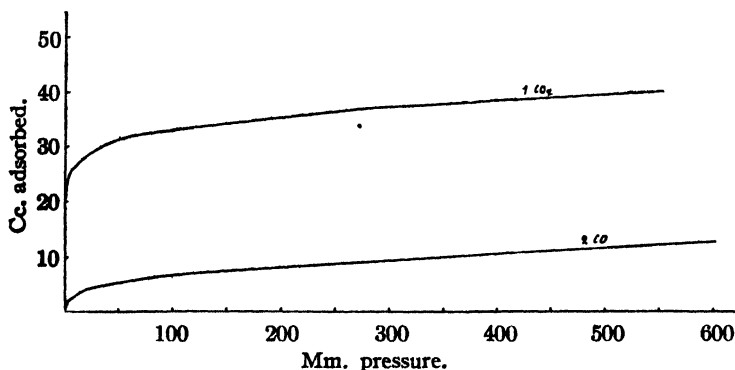


Fig. 5.

Fig. 5 shows the extraordinary adsorption of carbon dioxide by the zinc oxide catalyst. Thus the admission of 21.70 cc. of this gas to the catalyst at 100° produced a pressure of only 5 mm., and this pressure may be due in part to impurities, since tank carbon dioxide only was used; in the preceding runs with hydrogen and carbon monoxide the same amount of these gases had produced pressures of approximately 250 mm. This experiment confirms our observation in the evacuation process of the tenacity with which both carbon dioxide and water are adsorbed.

Discussion of Results

The experimental results demonstrate conclusively that zinc oxide and zinc oxide-chromium oxide catalysts show the same type of adsorption for the reactants of the methanol synthesis that is shown by metal catalysts in hydrogenation reactions. The type of adsorption isotherm is exactly the same in the two cases. There is strong adsorption at low pressures with relative saturation of the surface at these low pressures and little increase in adsorption with a many fold increase in pressure. This latter is readily appreciated by observing the nearly horizontal portions of the curves in the several diagrams.

The astonishing feature of the studies is, however, the extraordinary capacity of the catalysts for adsorption of the gases in question. They show many times the adsorptive capacity of the metal catalysts under the same conditions. This is readily seen from the appended Table I, which gives a few selected data of maximum adsorptions found in the earlier studies at Princeton on metal catalysts, under a variety of conditions, as well as some typical results from the present research.

TABLE I

Catalyst	ADSORPTIONS PER 100 G. OF CATALYST			Author
	Cc H ₂ adsorbed	Temp, °C.	Press., mm.	
Reduced copper	13.4	110	760	Taylor and Dew
Reduced copper	45	0	760	Taylor and Beebe
Reduced nickel	130	0	760	Taylor and Beebe
ZnO-Cr ₂ O ₃	184	100	1	Taylor and Kistiakowsky
ZnO	50	0	20	Taylor and Kistiakowsky

The table shows that at 100° and 1 mm. pressure a zinc oxide-chromium oxide catalyst has a greater adsorptive capacity for hydrogen than the best nickel catalyst we have ever prepared possesses at 0° and 760 mm., and a 13-fold better adsorptive capacity than a very active sample of reduced copper at 110° and 760 mm. pressure. The extremely high adsorptive capacity at low pressures thus revealed implies a very considerable amount of active catalytic surface per unit weight of material. This implies a corresponding insensitiveness to poisons and foreign materials in the gas mixture for such oxide catalysts. It may be concluded that such catalysts will tolerate concentrations of reversible poisons many fold greater than those which, with metal catalysts, produce a given diminution in catalytic activity. This is a very important industrial consideration.

Both the curves and the table show that the active surface in a mixed zinc oxide-chromium oxide catalyst is far greater than that of a corresponding weight of zinc oxide catalyst. There is, therefore, no element of surprise in the statements in both patent and technical literature that such mixed oxide catalysts are preferable to the single zinc oxide. Whether

the change in ratio of adsorption α_{H_2}/α_{CO} , with change from a single to a mixed oxide catalyst is significant in the synthesis of methanol cannot be deduced from these experiments. It will be noted that the ratio α_{H_2}/α_{CO} changes from approximately unity to approximately 0.5 at, for example, 100 mm. pressure. Whether this ratio change is significant may possibly be revealed by kinetic studies of the methanol process which are now in progress.

The very pronounced adsorption of carbon dioxide shown in Fig. 5, and the observation that both water vapor and carbon dioxide are so strongly retained by these catalysts that no measurable adsorptions were shown by samples evacuated at or below 300°, indicate that both gases are temporary poisons for these catalysts in methanol synthesis. It is significant that the activity of these methanol catalysts begins in the temperature range in which free evaporation of carbon dioxide and water vapor occur.

The rapid saturation of the surface at low pressures or the small change in total adsorption at higher pressures is characteristic of adsorptions involving high heats of adsorption. Rough calculations from the adsorption isotherms at 0 and 100° confirm this conclusion and indicate heats of adsorption of the same order of magnitude as are involved in adsorption of the gases on metal catalysts and considerably greater than the heats of liquefaction of the gases. We are attempting to measure these heats of adsorption directly to ascertain their precise magnitude and to discover whether they indicate special processes of activation.

The experiments recorded here are in complete harmony with the known activity of zinc oxide and zinc oxide-chromium oxide catalysts as agents for the synthesis of methanol. They suggest, however, a whole series of further investigations designed to ascertain why other oxides, for example magnesium oxide, cannot be utilized for such purposes with efficiency. The answer to such problems should promote a fuller understanding of the general problem of contact catalytic action. With some of these questions we are now engaged.

Summary

1. Adsorptions of hydrogen, carbon monoxide and carbon dioxide on two methanol catalysts, zinc oxide and zinc oxide-chromium oxide, have been measured at 0 and 100°.
2. It has been shown that, to obtain such measurements, the catalyst surface must be cleaned of adsorbed water vapor and carbon dioxide by evacuation at 400°.
3. It has been shown that both catalysts have adsorptive capacities per unit weight considerably greater than those of most metal catalysts.
4. The adsorption of both hydrogen and carbon monoxide is pro-

nounced at very low pressures and rapidly reaches saturation capacity independent of further pressure increase.

5. The experiments indicate that the heat of adsorption is considerably greater than the heat of liquefaction and attains values characteristic of heats of adsorption on metal catalysts.

6. The mixed oxide catalyst shows greater adsorptive capacity than the zinc oxide in harmony with its higher order of catalytic activity.

7. The experimental results generally are shown to be in agreement with the known facts concerning methanol synthesis on these catalysts.

PRINCETON, NEW JERSEY

THE STANDARDIZATION OF PROFESSOR T. W. RICHARDS'S THERMOCHEMICAL DATA

BY WOJCIECH SWIETOSLAWSKI AND J. BOBINSKA

RECEIVED JULY 20, 1927

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Professor T. W. Richards has authorized one of us to recalculate the values of the heats of combustion of organic compounds as examined by him, in order to standardize them and make them comparable with the standard unit now accepted in thermochemistry. As benzoic acid is established as this unit, the base for that comparison is the heat of combustion of 1 g. of benzoic acid weighed in a vacuum, 6319 cal. _{15°}, or 1 g. of this acid weighed in air, 6324 cal. _{15°}.

Discussing this question personally with Professor Richards, we accepted that, in the first column of each table containing the standardized thermochemical data, there must be cited the unchanged values, as given by the author in his original publication. Naturally, these values must be expressed in the same units used by the author. Therefore, we give in our two tables the values expressed in 18° calories or in kilojoules, respectively.

According to the different dates of publication, the measurements of Professor Richards are divided into two groups. The first series contains the determinations made with R. H. Jesse in 1910; the second one contains the rest, carried out after 1915, that is to say, after the appearance of Dickinson's investigations which established with great accuracy the heats of combustion of benzoic acid, cane sugar and naphthalene. This division is connected with the manner of determination of the heat capacity of the calorimetric system. In 1910, Professor Richards and R. H. Jesse carried out this determination using cane sugar as a standard substance. They accepted for the heat of combustion of this compound the value 16,545 kilojoules, proposed in 1909 by E. Fischer and Wrede. In the other papers, published after 1915, Professor Richards accepted the figures given by Dickinson.

The standardization of the data published after 1915 did not present any difficulty. In fact, Dickinson's values for the heats of combustion of benzoic acid, cane sugar and naphthalene had been accepted by the International Committee on Thermochemical Standards as the base for the establishment of the heat of combustion of benzoic acid. Therefore, the standardization in this case is a matter of expressing Professor Richards's data in terms of 15° calories instead of 18° calories or kilojoules, as was done in the original papers.

The coefficient rendering this recalculation possible is equal to 0.99942. It is calculated by using the following values of the mechanical equivalent of heat, determined by transforming electrical energy into heat at different temperatures.

Temp., °C.	Mech. equiv. of heat	Temp., °C.	Mech. equiv. of heat
15	4.1843	18	4.1819
16	4.1835	19	4.1812
17	4.1827	20	4.1805

The corresponding coefficient enabling us to standardize the data published in Professor Richards's first paper (1910) has been determined by comparing the values given by Fischer and Wrede for the heats of combustion of cane sugar and naphthalene with the figures established lately with great precision by several authors (Dickinson, Verkade, Swietoslawski and Starczewska and Schläpfer).

It has been shown by Swietoslawski,¹ in several papers concerning the establishment of a thermochemical standard unit, that the above-mentioned data of Fischer and Wrede are too high by +0.3%. The following comparison gives directly the value of the coefficient which ought to be accepted for the recalculation of the Richards data published in 1910.

Compound	Formula	Fischer and Wrede [KJ]	Standardized data [KJ]	Stand. data
				Fischer and Wrede
Naphthalene	C ₁₀ H ₈	40,314 ^a	40,179	0.9967
Cane sugar	C ₁₂ H ₂₂ O ₁₁	16,545 ^b	16,501	0.9973
				Average value 0.9970

^a Wrede

^b Fischer and Wrede (2).

When the above-mentioned values have been expressed in kilojoules, the coefficient 0.9970 must be multiplied by 1000 and divided by 4,1843; $\alpha = (0.9970 \times 1000)/4.1843 = 238.27$.

In the two tables the first column contains the name of the substance with reference to original publication; the second, the formula; the third, the molecular weight *M*; the fourth, the heat of combustion of 1 g.

¹ Swietoslawski, *J. chim. phys.*, **22**, 391, 396, 399, 583 (1925); *Bull. soc. chim.*, (4) **37**, 84 (1925); *Bull. Acad. Polonaise Sc.*, (A) 1927, 42, 43, 54.

(vac.) of substance ($v = \text{const.}$) expressed in kilojoules $A(KJ)$; the fifth, the same values expressed in calories $A_{\text{cal. 18}^\circ}$; the sixth, the corresponding standardized values A ; the seventh and the eighth, the molecular heat of combustion of the substance at constant volume A_v and at constant pressure A_p .

TABLE I
THE COEFFICIENT OF STANDARDIZATION 238.27

Substance ^a	Formula	M	A (KJ)	A (cal 18°)	A	A _v	A _p
<i>n</i> -Octane.....	C ₈ H ₁₈	114.14	47.73	11,372.6	1298.1	1300.7
2,5-Dimethylhexane.....	C ₈ H ₁₈	114.14	47.68	11,360.7	1296.7	1299.3
2-Methylheptane....	C ₈ H ₁₈	114.14	47.78	11,384.5	1299.4	1302.0
3,4-Dimethylhexane.....	C ₈ H ₁₈	114.14	47.70	11,365.5	1297.3	1299.9
3-Ethylhexane.....	C ₈ H ₁₈	114.14	47.65	11,353.6	1295.9	1298.5
Benzene.....	C ₆ H ₆	78.05	41.99	10,048	10,005.0	780.9	781.8
<i>o</i> -Xylene.....	C ₈ H ₁₀	106.08	43.10	10,269.4	1089.4	1090.8
<i>m</i> -Xylene.....	C ₈ H ₁₀	106.08	43.10	10,269.4	1089.4	1090.8
<i>p</i> -Xylene.....	C ₈ H ₁₀	106.08	42.95	10,233.7	1085.6	1087.0
Methyl isobutyrate..	C ₅ H ₁₀ O ₂	102.08	28.419	6,771.4	691.2	692.1

^a Richards and Jesse, THIS JOURNAL, 32, 268 (1910).

TABLE II
THE COEFFICIENT OF STANDARDIZATION, 0.99942

Substance	Formula	M	A (KJ)	A (cal 18°)	A	A _v	A _p
Di- <i>iso</i> -amyl ^a	C ₁₀ H ₂₂	142.18	...	11,339	11,332.4	1611.2	1614.4
Benzene ^a	C ₆ H ₆	78.05	...	10,014	10,008.2	781.1	782.0
Benzene ^b	C ₆ H ₆	78.05	41.79	9,993	9,987.2	779.5	780.4
Toluene ^b	C ₇ H ₈	92.06	42.51	10,166	10,160.1	935.3	936.5
Toluene ^a	C ₇ H ₈	92.06	...	10,155	10,149.1	934.3	935.5
<i>o</i> -Xylene ^b	C ₈ H ₁₀	106.08	42.98	10,277	10,271.0	1089.	1090.9
<i>m</i> -Xylene ^b	C ₈ H ₁₀	106.08	42.98	10,277	10,271.0	1089.	1090.9
<i>p</i> -Xylene ^b	C ₈ H ₁₀	106.08	42.83	10,241	10,235.1	1085.	1087.1
Ethylbenzene ^b	C ₈ H ₁₀	106.08	42.96	10,273	10,267.0	1089.	1090.5
Mesitylene ^b	C ₉ H ₁₂	120.10	43.24	10,340	10,334.0	1241.	1242.8
<i>n</i> -Propylbenzene ^b	C ₉ H ₁₂	120.10	43.34	10,364	10,358.0	1244.0	1245.7
Isopropylbenzene ^b	C ₉ H ₁₂	120.10	43.37	10,371	10,365.0	1244.8	1246.5
Pseudocumene ^b	C ₉ H ₁₂	120.10	43.14	10,316	10,310.0	1238.2	1239.9
<i>Tert.</i> -butylbenzene ^a ...	C ₁₀ H ₁₄	134.11	...	10,434	10,427.9	1398.5	1400.5
<i>Tert.</i> -butylbenzene ^b ...	C ₁₀ H ₁₄	134.11	43.60	10,427	10,421.0	1397.6	1399.6
Cyclohexane ^b	C ₆ H ₁₂	84.10	46.69	11,164	11,157.5	938.3	940.0
Methyl alcohol ^a	CH ₄ O	32.03	...	5326	5322.9	170.5	170.8
Ethyl alcohol ^a	C ₂ H ₅ O	46.05	...	7101	7096.9	326.8	327.4
Propyl alcohol ^a	C ₃ H ₇ O	60.06	...	8033	8028.3	482.2	483.1
Butyl alcohol ^a	C ₄ H ₁₀ O	74.08	...	8615	8610.0	637.8	639.0
Isobutyl alcohol ^a	C ₄ H ₁₀ O	74.08	...	8599	8594.0	636.6	637.8
Cyclohexanol ^a	C ₆ H ₁₂ O	100.10	...	8882	8876.8	888.6	890.0

^a Richards and Davis, THIS JOURNAL, 42, 1599 (1920).

^b Richards and Barry, *ibid.*, 37, 993 (1915).

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF COMMERCE, BUREAU OF MINES,
PITTSBURGH EXPERIMENT STATION, CHEMICAL DIVISION]

IGNITION OF NATURAL GAS-AIR MIXTURES BY HEATED METAL BARS¹

BY H. F. COWARD² AND P. G. GUEST³

RECEIVED JULY 30, 1927

PUBLISHED OCTOBER 5, 1927

This communication records certain observations, of general scientific interest, concerning the influence of catalytically active surfaces on the ignition temperature of gas mixtures. The work is preliminary to a technical study of the possibilities that heated metal may directly or indirectly initiate gas explosions in coal mines.

The experimental work was conducted by the junior writer in the Electrical Section of the Pittsburgh Experiment Station of the Bureau of Mines at the instigation and under the general supervision of L. C. Ilsley, electrical engineer.

Influence of Solids on the Ignition of Gases

It was long ago observed that the apparent ignition temperature of an explosive gas mixture was raised by increase of the area of a solid body exposed to it, as, for example, by packing the containing vessel with fragments of glazed porcelain.⁴ This was ascribed to the retardation which the solid exerts on the self-heating of the gas mixture; for if the vessel and its contents are at the same temperature, self-heating of the gas by its own combustion is more difficult the more there is of solid material exposed to absorb the thermal energy of the combustion.

When, however, the solid has a marked catalytic action, this might be expected to reduce the ignition temperature; the ignition of a jet of cold hydrogen when it has streamed for a few moments over platinized asbestos apparently confirms this expectation. On the other hand, the experiments reported herein show that a powerfully catalytic surface has to be far hotter to ignite an explosive mixture of natural gas and air than has a surface of equal dimensions but of small catalytic action. Furthermore, those mixtures of natural gas and air which are most violently explosive require the highest temperatures for ignition by a heated bar of catalytically active metal (platinum).

The new observations are not in conflict with that of the ignition of hydrogen by platinized asbestos, for this solid has relatively little mass, in comparison with its surface area, and becomes red- or white-hot before

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⁴ Hélier, *Ann. chim. phys.*, [7] 10, 521 (1897).

the gas in its interstices ignites. The metal bars used in the present experiments have so great a heat capacity that their temperature is but little affected by combustion around them. They behave rather as thermostats, whereas the platinized asbestos rapidly rises in temperature, accumulating heat from the gas first burning by slow combustion and thereby increasing the rate of burning of gas arriving subsequently.

Experimental

Strips of metal were heated electrically in the center of a gas-tight, rectangular gallery of about 4.5 cu. ft. capacity. The dimensions of the metal strips or bars were varied in some of the tests, but for comparison between different metals a standard size of 4.25 inches long (between the terminal clamps), 0.50 inch wide and 0.040 inch thick was chosen. At the high temperatures required for ignition, a length of about an inch at the center of the bar was found to be uniformly heated. Its temperature was observed by means of a thermocouple peened into the bar, and careful tests showed that when the couple was properly inserted the alternating current used in heating the bar did not interfere with the thermocouple current.

The gallery was fitted with a large release valve of waxed paper which burst when an explosive mixture was ignited. It also contained a large fan, used to ensure homogeneity of the gas mixture, and a smaller fan which was used in some experiments on the influence of turbulence on ignition.

The explosive gas mixtures used were composed of natural gas and air. The composition of the former was fairly constant during the series of experiments and averaged 93.2% CH_4 , 3.3% C_2H_6 , 1.5% C_3H_8 , 0.5% C_4H_{10} , etc., and 1.5% N_2 . The gas admitted to the gallery was measured approximately by means of a standard wet-type gas meter. When the gas and air had been well mixed by the fan, a sample was withdrawn and analyzed by the thermal conductivity method. Either gas or air was then admitted as required until the desired mixture was obtained. Occasional checks on the accuracy of the gas analysis, by comparing the thermal conductivity results with those obtained by a combustion analysis, were satisfactory.

When the atmosphere in the gallery had been prepared, the bar was rapidly heated to a few degrees short of the temperature at which, according to previous trials, ignition might be expected. The rate of rise of temperature was then somewhat retarded and the potentiometer used in connection with the thermocouple was adjusted continuously for zero galvanometer reading until ignition took place. Practice enabled the investigator to raise the temperature of the bar to the ignition point with sufficient rapidity to avoid any sensible change in the composition of the

gas mixture in the gallery, and yet not too rapidly for the temperature of ignition to be noted accurately. The gallery was large enough to provide latitude in the duration of the heating period, and constant results were obtained within a wide range of variation of rate of heating.

The choice of metals suitable for experiment is limited; the metal must have a high melting point and must not oxidize too rapidly at temperatures well above 1000° . On account of rapid oxidation and irregular scaling, iron failed to give reproducible results, although samples from several sources were tried. Certain steels, copper and Monel metal were more regular but melted at temperatures which restricted their utility. Stainless steel and a British steel of special composition, which resists oxidation at high temperatures, gave reproducible results. Platinum and nickel were found to be the most satisfactory materials for use in a long series of tests, and the latter was adopted as a standard of comparison.

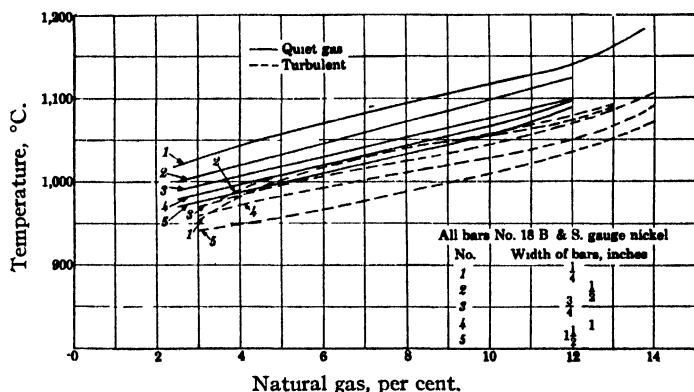


Fig. 1.—Ignition of natural gas and air mixtures by heated nickel bars.

The range in composition of the mixtures which are reported as "ignited" lies between 2.4 and 16% of natural gas. Ignition of mixtures near to the two limits was indicated by the sudden appearance of a cap of flame above the bar and an increase of pressure as shown on a manometer. It was only between the limits of 5.5 and 13.5% natural gas that the inflammation spread from the bar through most or all of the gas mixture.

Results of Experiments

1. Nickel Bars: Effect of Change of Bar Dimensions.—Nickel bars of various widths⁵ were placed in the terminal clamps within the gallery in such a manner that their axes of length and thickness were horizontal, that is, they were on edge and the vertical dimension was varied. Fig. 1 shows the minimum temperatures at which the various bars ignited the

⁵ These were cut from the same sheet of commercial nickel.

whole series of natural gas-air mixtures. The solid-line curves represent the results obtained when there was no mass movement of the gas other than that caused by convection currents about the heated bar. The broken curves represent results obtained in gas agitated by the rapid revolution of the small fan mounted several inches above the bar.

It is clear that the temperature necessary to ignite these mixtures by nickel bars increases with increase in natural-gas content of the mixture. No certain explanation for this is at present available.⁶ The wider bars ignite the various mixtures more readily than the narrower bars; for the streaming gas is exposed for a longer period to the source of heat when in contact with the wider bars. Such turbulence as was imparted by the fan served to reduce the temperature necessary for ignition; but experiments now in progress show that when the turbulence is sufficiently great the opposite effect is produced.

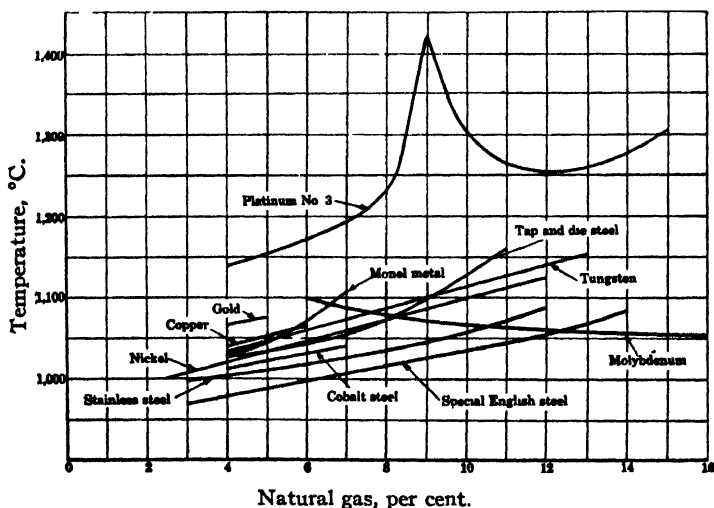


Fig. 2.—Ignition of natural gas mixtures by heated bars of various metals.

The limits of temperature at which ignition occurred with bars ranging between 0.25 and 1.5 inches in width, mixture composition between 2.5 and 14%, with and without turbulence, were 940 and 1180°. This range is widened by more extreme variations in the experimental conditions. For example, a thin nickel bar bent into the form of a slotted tube gave a value as low as 724°. The figures must, therefore, be regarded as relative, rather than absolute.

A few tests made with methane for comparative purposes showed that

⁶ For a suggestion, made in connection with somewhat similar results observed in quartz vessels, see S. C. Lind, *J. Chem. Soc.*, 125, 1867 (1924).

this gas, in contact with nickel, ignites at temperatures about 30° higher throughout the range of mixtures.

2. Effect of Different Metals on Ignition Temperatures.—Fig. 2 shows the minimum temperatures at which bars of various metals ignited the series of natural gas-air mixtures. As already stated, all the bars were of the same dimensions and were mounted as described in (1).

It appears (see also Fig. 3) that the various steels, copper, Monel metal and gold do not differ nearly so much in their ability to ignite the gas as the catalytically active metals platinum and palladium differ from nickel;

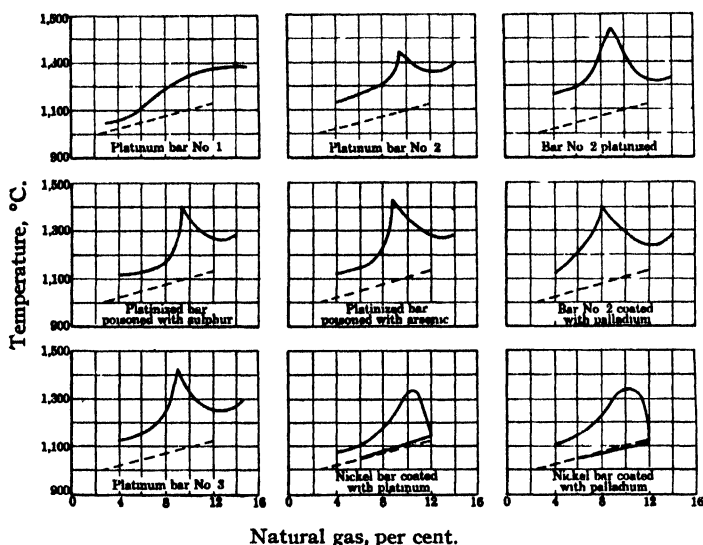


Fig. 3.—Ignition of natural gas-air mixtures by heated platinum and palladium surfaces. (The broken line in this figure represents the corresponding observations with a nickel bar.)

and three samples of platinum differed widely from one another. The abnormal character of the molybdenum curve is doubtless associated with the rapid burning of the metal; dense clouds of oxide were formed in all experiments. Tungsten did not give rise to an oxide cloud until raised to temperatures higher than any required for ignition of the gas mixtures.

Fig. 3 shows that while platinum sample No. 1 had to be much hotter than nickel in order to ignite the gas, the two curves are of similar type. Samples⁷ No. 2 and 3, however, showed a remarkable peak in the neigh-

⁷ We are indebted to the American Platinum Company for the following analysis of platinum bar No. 3: Pt, 99.51%; Ir, nil; Pd, 0.32%; Rh, 0.11%; Au, nil. The first bar had been remelted with other scrap metal before the desirability of an analysis was recognized.

borhood of the most violently explosive mixtures of gas and air, namely, those which contain just over 9% of natural gas.⁸ Wüllner and Lehmann⁹ record a similar result with a platinum wire of 0.5 mm. diameter suspended in methane-air mixtures. A stouter wire, also a platinum gauze, failed to show a maximum temperature for ignition in their other series of experiments.

Further experiments with platinum bar No. 2 showed that this effect could be increased by electrolytically depositing finely divided platinum or palladium upon the surface of the bar, and thereafter could be decreased somewhat by treating the bar with such catalytic poisons as arsenic and sulfur. These poisons burned off, however, after the first few ignitions and the characteristics previously showed by the bar were restored.

That the most explosive mixture should require the highest temperature for ignition by these two bars is evidence that the specific action of platinum is to be ascribed to its high catalytic activity in comparison with the weaker action of nickel and the other metals tested. In support of this contention is the variability of platinum bar No. 2 with chemical treatment and the dissimilarity of the curve for platinum bar No. 1. The consistency of the nickel results, in conjunction with the variability of the platinum results (as between the three samples), is what would be expected if platinum were the material subject to the vagaries of a catalyst and nickel were little more (in the case of natural gas and air) than a source of heat without much catalytic effect.

Further evidence in support of this view is also shown in Fig. 3. Two nickel bars were used, one coated with platinum and the other with palladium. Observations were made with increasing amounts of natural gas, and the upper parts of the two curves were obtained. In each case, after the observation with the 11% gas mixture, the subsequent figures (plotted in the lower part of the curve) followed closely the nickel curve. Doubtless the rare metal had dissolved and passed into the mass of the nickel when this occurred.

If it is correct to ascribe the high ignition temperature obtained with platinum to its high catalytic activity, direct evidence should be obtainable from an examination of the gases exposed to the hot metals. Parallel experiments were therefore made in which nickel and platinum bars were separately placed in mixtures containing 9% of natural gas and carefully maintained at 1050° for periods of 8 and 20 minutes. The results of the analyses of samples then taken after thoroughly mixing the gallery atmosphere with the fan were as follows.

⁸ The "theoretical" mixture of natural gas and air, which has just sufficient oxygen to burn the gas completely, contains 9.09% of natural gas. Flame is propagated most rapidly in mixtures which are slightly richer than this. See ref. 11.

⁹ Wüllner and Lehmann, "Anlagen zum Hauptbericht der Preussischen Schlagwetter Commission," 1886, p. 219.

COMBUSTION OF GASES DURING PRE-FLAME PERIOD		
Gas present	With platinum bar, %	With nickel bar, %
Natural gas, at start	9.1	8.99
CO ₂ , after 8 minutes	1.01	0.05
CO, after 8 minutes	0.72	.50
Natural gas, at start	8.75	8.77
CO ₂ , after 20 minutes	1.96	0.07
CO, after 20 minutes	0.22	.36

It will be seen that more than 20 times as much carbon dioxide was formed with the platinum bar as was formed with the nickel at the same temperature.

In all the higher percentage mixtures employed, when the mixture was not inflamed, quiet combustion around the platinum maintained its temperature above red heat for several minutes after the heating current had been shut off. This was not observed at any time with the nickel bar and is further evidence, if any were needed, of the superior catalytic action of platinum at high temperatures on natural gas-air mixtures.

3. Comparative Experiments with Nickel and Quartz.---It is generally accepted that fused quartz has relatively little catalytic action on the combustion of the paraffin hydrocarbons.¹⁰ If, then, nickel and fused quartz should give similar results in similar circumstances, it might be concluded that nickel also had little catalytic action on the combustion of natural gas. As it was not possible to heat a quartz bar by the same means as the metal bars had been heated, a comparison of the ignition temperatures in tubes was adopted. The ignition temperature of natural gas in a certain quartz tube was about 620° and varied but little over the whole range of inflammable mixture.¹¹

Tubular vessels of length and diameter equal to the quartz tube were made from two samples of nickel sheet and were heated by the same means as had been used for the metal bars in the same chamber. A narrow slit was left along the bottom of each tube and when ignition occurred within, flame was seen to be projected through the slit and to ignite the main mass of gas outside. In these circumstances the range of ignition temperatures for mixtures containing from 4 to 12% of natural gas was 832 to 878° in one tube, 724 to 800° in another. It had been expected that much lower ignition temperatures would be obtained for the nickel tubes than for the nickel bars, for Mallard and Le Chatelier¹² had found that methane was ignited by a heated iron crucible at a much lower temperature when the gas was allowed to stream up into the in-

¹⁰ See, for example, H. B. Dixon and H. F. Coward, *J. Chem. Soc.*, 95, 514 (1909). W. Mason and R. V. Wheeler, *ibid.*, 121, 2079 (1922); 125, 1869 (1924).

¹¹ Coward, Jones, Dunkle and Hess, *Bull. 30, Carnegie Inst. of Tech.*, "The Explosibility of Methane and Natural Gas," 1926, 42 pp.

¹² Mallard and Le Chatelier, *Ann. des Mines*, [8] 4, 274 (1883).

verted crucible than when the gas streamed up around the outer surface of the crucible in its normal position. This they explained on the basis of the effect of convection currents in removing hot gases before the end of the "time lag" prior to inflammation. The figures obtained with the two tubes used in the present experiments differed somewhat widely; the difference may be due to some difference in shape or in material, although bars cut from the two samples of nickel sheet gave almost identical figures. However that may be, it is clear that in a comparison between quartz and nickel surfaces, the quartz surface of small catalytic action gives the lower ignition temperature. In view of this, and in the light of the conclusions drawn regarding the high catalytic action of platinum, it must be concluded that nickel itself has a significant catalytic action on the combustion of natural gas.

The most probable explanation of the apparent paradox (that catalytic action of a solid surface tends to raise the ignition temperature of a gaseous mixture) can hardly be given better than in the words of Mason and Wheeler.¹⁰

"The mixture immediately surrounding the heated surface may be consumed so rapidly as to become incapable of propagating flame, the reaction continuing to take place only at or near the heated surface even though its temperature there may rise far above the true ignition temperature of the mixture."

The effect of moderate turbulence must be to bring inflammable gas into the zone of burnt-out mixture, and thus to raise its temperature, perhaps to the ignition point, when it is near but not on the heated surface.

Summary

Measurements of the temperatures at which metal bars ignite mixtures of natural gas and air show that:

1. In parallel experiments the metals of greater catalytic effect must be hotter to cause ignition than metals or other substances of smaller catalytic effect. The difference may be several hundred degrees.

2. The temperature necessary to ignite these mixtures by bars of nickel, tungsten and several special steels increased regularly with increase in natural gas content throughout the whole range of inflammable mixtures.

3. With two of the three platinum bars tested, a much higher temperature was required to ignite the most violently explosive mixtures than was required to ignite mixtures of less explosibility.

A record is also given of the effect of variations in dimensions of the heated bar and of the effect of moderate turbulence on the ignition of these gaseous mixtures.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

TERNARY SYSTEMS. VI. SODIUM CARBONATE, SODIUM BICARBONATE AND WATER

BY ARTHUR E. HILL AND LESLIE R. BACON¹

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It has been known for a very long time that solutions of carbonate and bicarbonate of sodium may precipitate the double salt Trona as well as the two simple salts. The concentrations and temperatures at which these compounds separate have not, however, been investigated except in a single instance; McCoy and Test² have studied the three-component isotherm at 25°, giving the results in terms of volume concentration. We have here studied the system at the temperatures 25, 30 and 50°, determining the composition of the saturated solutions by weight and their density.

Experimental Methods.—The sodium carbonate and bicarbonate used were Kahlbaum's "zur Analyse" preparations; the former was found to be 100% in purity, and was kept constantly in an electric oven at 100° until removed for use. The samples of bicarbonate were found to contain from 1.30 to 3.16% of normal carbonate and from 0.33 to 0.70% of water. Because the conditions for keeping the bicarbonate from change are not known, the samples were used without removing the carbonate, making proper corrections for their actual composition in the various experiments.

Solubilities were obtained in thermostats, using 50 cc. glass-stoppered Pyrex tubes, the stoppers being wired in to prevent loss of carbon dioxide during stirring. Rotation was continued until equilibrium was obtained, the usual period being about fifteen hours. Samples for analysis were removed with a pipet fitted with a filter, and weighed to give a fairly accurate density determination. The loss of carbon dioxide, which Dibbitts³ points out as considerable for solutions saturated with sodium bicarbonate, is very little in the presence of even small amounts of the normal carbonate; no especial precautions were necessary on this account. One sample of filtrate was titrated with 0.5 *N* hydrochloric acid, using methyl orange as indicator, to determine the total base; a second sample was analyzed for carbon dioxide content by absorption in soda lime in a Morgan bottle, thus permitting calculation of the concentration of both normal salt and acid salt. The thermometers were compared with a standard thermometer.

¹ The material of this paper is part of a thesis presented by Leslie R. Bacon in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at New York University.

² McCoy and Test, *THIS JOURNAL*, **33**, 473 (1911).

³ Dibbitts, *J. prakt. Chem.*, **10**, 417 (1874).

The Binary Systems.—For the two binary systems, only the eutectics were determined, as the solubility data in the literature appear to be accurate. In the case of the bicarbonate, the usual method of lengthy stirring in open vessels was found to result in considerable loss of carbon dioxide and the formation of normal carbonate. To avoid this error, washed carbon dioxide was passed into the solution during the determination of the eutectic in the Beckmann apparatus; the correction for freezing-point depression caused by saturation with the gas is only a few hundredths of a degree. The results are given in the following table.

TABLE I
BINARY EUTECTICS FOR Na_2CO_3 AND NaHCO_3 WITH H_2O

Point in Fig. 4	Eutectic temp.	Solution		Density	Solid phases
		Wt. %, Na_2CO_3	Wt. %, NaHCO_3		
B	-2.05	5.71	..	1.056	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{ice}$
M	-2.33	..	6.26	1.046	$\text{NaHCO}_3 + \text{ice}$

The eutectic for the bicarbonate we have not found in the earlier literature. That determined by us for the normal carbonate is slightly lower in temperature and concentration than that given by Guthrie⁴ (-2.0° and 5.97%) and is higher in concentration than the value given by de Coppet⁵ (-2.1° and 5.03%); it is much closer to the extrapolated solubility curve than either of these earlier results.

The Ternary Isotherms.—In Tables II, III and IV are given the data for the ternary system at 24.87, 30.0 and 50.0°. The water in the saturated solutions may be calculated by subtracting the sum of Cols.

TABLE II
ISOTHERM AT 24.87° FOR $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + \text{H}_2\text{O}$

Point in figs.	Solution			Original complex		Solid phases
	Wt. %, Na_2CO_3	Wt. %, NaHCO_3	Density	Wt. %, Na_2CO_3	Wt. %, NaHCO_3	
A	0.0	(9.3)	N_{bi}
	0.2	9.11	1.065	N_{bi}
	2.10	8.21	1.076	1.91	17.29	N_{bi}
	8.11	6.13	1.125	7.45	14.05	N_{bi}
	10.88	5.50	1.152	10.08	12.46	N_{bi}
	13.61	4.90	1.179	12.57	12.41	N_{bi}
K	17.85	4.00	1.216	$\text{N}_{bi} + \text{T}$
	18.66	3.57	1.225	21.26	6.46	T
	19.31	3.18	1.228	21.17	6.54	T
	20.90	2.49	1.240	23.30	6.12	T
C	22.10	2.09	1.250	$\text{T} + \text{N}_{10}$
	22.15	1.59	1.247	26.31	1.23	N_{10}
	22.26	1.09	1.243	26.03	1.04	N_{10}
	22.20	0.86	1.238	26.06	0.51	N_{10}
D	22.45	.00	N_{10}

⁴ Guthrie, *Phil. Mag.* [4] 49, 269 (1875).

⁵ De Coppet, *Z. physik. Chem.*, 22, 240 (1897).

TABLE III
 ISOTHERM AT 30.00°

Point in figs.	Solution		Density	Original complex		Solid phases
	Wt. % Na_2CO_3	Wt. % NaHCO_3		Wt. % Na_2CO_3	Wt. % NaHCO_3	
A	0.0	(9.8)	N_{bi}
	0.25	9.71	1.068	N_{bi}
	6.06	7.30	1.112	5.38	18.03	N_{bi}
	11.84	5.67	1.160	10.33	17.68	N_{bi}
K	17.52	4.45	1.216	$\text{N}_{bi} + \text{T}$
	18.43	3.92	1.225	19.98	5.87	T
	18.54	3.91	1.226	20.09	5.66	T
	21.00	2.65	1.239	22.45	4.80	T
	23.39	1.79	1.256	24.01	2.95	T
	24.30	1.47	1.269	25.88	4.32	T
	27.52	0.82	1.301	29.06	3.91	T
	28.09	.76	1.307	T + N_{10}
D	28.24	.00	1.296	N_{10}

 TABLE IV
 ISOTHERM AT 50.00°

Point in figs.	Solution		Density	Original complex		Solid phases
	Wt. % Na_2CO_3	Wt. % NaHCO_3		Wt. % Na_2CO_3	Wt. % NaHCO_3	
A	...	(12.40)	N_{bi}
	0.27	12.22	1.078	N_{bi}
	1.08	11.68	1.079	N_{bi}
	4.78	9.93	1.112	N_{bi}
	10.04	8.27	1.152	9.20	17.10	N_{bi}
	14.90	6.80	1.196	13.39	15.73	N_{bi}
K	16.97	6.28	1.214	$\text{N}_{bi} + \text{T}$
	23.79	2.40	1.260	25.59	5.21	T
C	31.92	0.48	1.337	T + N_1
D	32.16	.00	1.331	N_1

2 and 3 from 100%. As abbreviations for the compositions of the solid phases given in the last column, N_{10} , N_7 and N_1 are used for the decahydrated, heptahydrated and monohydrated sodium carbonate, respectively, N_{bi} for the bicarbonate and T for the double salt, Trona, $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$. Figs. 1, 2 and 3 represent the results graphically.

Lines drawn through the two points representing the saturated solution and the original complex can be extrapolated to pass through the point representing the saturating solid phase with sufficient accuracy.

From the foregoing data, it can be shown that the solubility of the normal carbonate is increased slightly by the addition of bicarbonate, if calculated as referred to a constant amount of water; this is the case for the course of the short solubility curve DC. The solubility of the bicarbonate, however, as indicated by the curve AK, shows the more usual behavior of a marked decrease in solubility upon the addition of the carbonate. The solubility of the pure bicarbonate, given at A in the three isotherms,

satisfied ourselves as to the correctness of this formula by two independent methods. The first consisted in a slow isothermal evaporation over sulfuric acid at about 30° , using a solution represented by a point on the solubility curve CK, discontinuing before the total composition of the system had moved outside the triangle TCK; the slow procedure gave relatively distinct crystals (although we have not been able to obtain them of any large dimensions) which could be well centrifuged. Analysis of three samples gave the water content 1.43% too great, the bicarbonate 1.05% too small and the carbonate 0.38% too small for the above formula. The second method consisted in preparing two saturated solutions, to one of which the three components were added in the molecular ratio

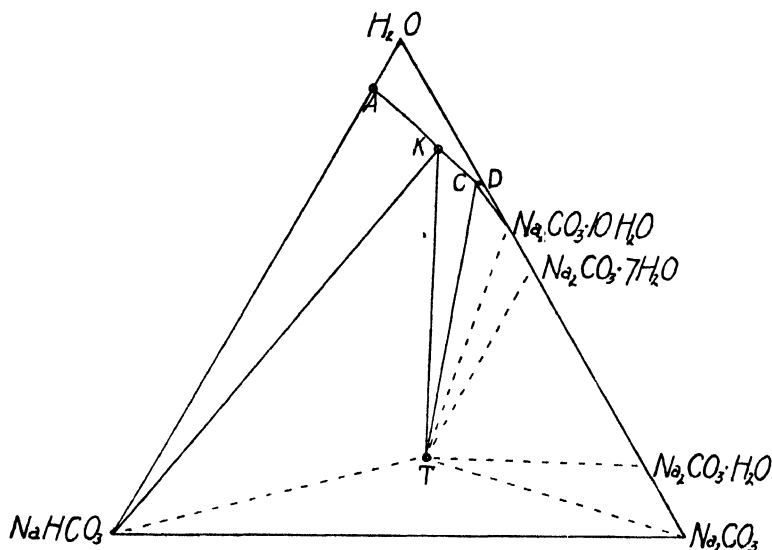


Fig. 2.—Isotherm for $\text{Na}_2\text{CO}_3\text{--NaHCO}_3\text{--H}_2\text{O}$ at 30° .

$\text{NaHCO}_3 + \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$ and to the second in the ratio $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$; in the first experiment the composition of the saturated solution moved in the direction toward K, and in the second toward C, indicating that the first addition contained water in excess and the second in deficit.

The range of concentrations within which Trona is stable varies widely with the temperature. At 25° the triangle TKC is quite narrow, indicating that the compound is here but slightly above its temperature of formation; the determination of that temperature is given later in the paper. The points C and K agree with those of McCoy and Test² within less than 0.2%, the comparison being made possible by the density data contained in our tables. At 30° the triangle TKC has extended considerably, and at 50° is still larger. It seems probable, therefore, that Trona

may be stable up to considerably higher temperatures, provided the pressure is kept high enough to prevent the loss of carbon dioxide. The salt shows incongruent solubility throughout the temperature range studied; but it should be observed that with increasing temperature there is a continuous movement of the point K toward A, and it is not by any means excluded that at sufficiently high temperature and pressure it may move far enough to bring the salt into congruent saturation, so that it might be recrystallized from water.

The point C represents solutions isothermally saturated with Trona and with sodium carbonate decahydrate in Tables II and III, and with Trona

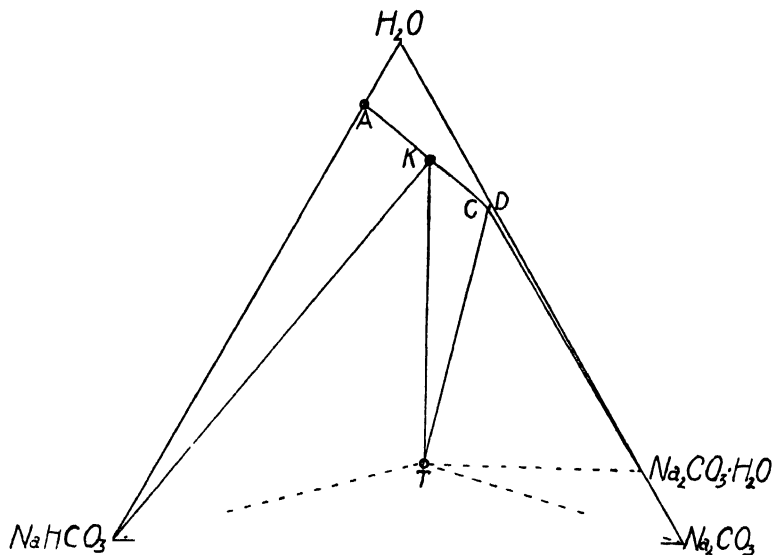


Fig. 3.—Isotherm for $\text{Na}_2\text{CO}_3\text{--NaHCO}_3\text{--H}_2\text{O}$ at 50° .

and sodium carbonate monohydrate in Table IV; at temperatures between 31.98 and 35.27° , as shown later in this paper, the two salts will be Trona and sodium carbonate heptahydrate. In every case the point is close to the $\text{H}_2\text{O--Na}_2\text{CO}_3$ axis, its farthest removal being 3.74% at 21.26° and its closest approach being 0.16% at 31.98° . It is apparent from these figures that a comparatively small addition of bicarbonate to normal carbonate will result in the precipitation of Trona, and that pure carbonate cannot be prepared by recrystallization if the excess of carbon dioxide is more than a very small amount.

The Invariant Points (Quintuple Points).—With the number of possible solid phases at moderate temperatures so large ($\text{Na}_2\text{CO}_3\text{--H}_2\text{O}$, $\text{Na}_2\text{CO}_3\text{--}7\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3\text{--}10\text{H}_2\text{O}$, NaHCO_3 , Trona and ice) it is obvious that several invariant (quintuple) points might be expected. Investigation from the temperature of the ternary eutectic up to 50° has given four such

invariant points, the data for which are in Table V. L stands for the saturated liquid phase. The phase reaction, read from left to right, represents the change occurring upon addition of heat.

TABLE V
INVARIANT POINTS IN THE SYSTEM $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$

Point in Fig. 4	Temp., °C.	Liquid phase		Density	Phase reaction
		Wt. %, Na_2CO_3	Wt. %, NaHCO_3		
E	-3.32 ± 0.05	4.41	4.64	1.078	$\text{N}_{10} + \text{N}_{bi} + \text{ice} \rightleftharpoons \text{L}$
H	$+21.26 \pm .10$	18.15	3.74	1.220	$\text{N}_{10} + \text{N}_{bi} \rightleftharpoons \text{T} + \text{L}$
N	$31.98 \pm .05$	31.32	0.16	1.334	$\text{N}_{10} + \text{T} \rightleftharpoons \text{N}_7 + \text{L}$
O	$35.17 \pm .05$	33.08	.19	1.350	$\text{N}_7 + \text{T} \rightleftharpoons \text{N}_1 + \text{L}$

The invariant temperature of Line 1 was determined with the usual Beckmann apparatus; the heat of the reaction is large and if vigorous stirring and a slow drop of temperature are maintained, the transition temperature is reproducible with satisfactory accuracy. In the other experiments, however, each of which involves the formation or decomposition of Trona, special precautions were necessary to avoid considerable variations in the transition temperature. This was especially true of the experiment of Line 2, which is the temperature of formation of Trona from its components previously referred to, and found to be at 21.26° . The temperature found is in agreement with the finding of McCoy and Test² that Trona is a stable phase at 25° , and with that of Applebey and Lane³ that the compound is non-existent at 18° . The use of the ordinary Beckmann apparatus, however, gave no satisfactory determination of the temperature; cooling curves and heating curves showed arrests differing a degree or more from each other, and yielding no truly invariant temperature, from which it may be deduced that the heat of the reaction is small or that the rate of formation and decomposition of the double salt is slow, or possibly that both statements may be true. In order to obtain a satisfactory curve, it was necessary to carry on the experiments in a small Dewar flask, surrounded by water at a temperature only a degree or two above the invariant temperature, and to carry on mechanical stirring over a period approximating a day, seeding the mixture with the necessary salts. With the exceedingly slow change in temperature thus produced, a constant temperature was obtained over a period of several hours; the average of four such determinations is given. The determinations of Lines 3 and 4 were somewhat less troublesome but the use of the Dewar flask as a container was found necessary. Since in these two latter cases the concentration of bicarbonate in the solution is very small, it is clear that the transition points can vary only slightly from the two-component transition temperatures of the heptahydrated and decahydrated carbonates. These two-component temperatures were therefore redetermined by us so that

³ Applebey and Lane, *J. Chem. Soc.*, 113, 609 (1918).

our three-component temperatures should express a difference brought about by the presence of the bicarbonate rather than a variation between the work of different investigators. By our experiment the transition temperature of sodium carbonate decahydrate was found to be 32.08° ,⁹ making the depression by the bicarbonate 0.1° , and that of the heptahydrate was found at 35.27° , making the depression by the bicarbonate again 0.1° .

From the solubility data and the invariant points it is possible to construct a space model showing relationships in the ternary system from -3.32° to $+50^\circ$. This is shown in perspective in Fig. 4, which is drawn

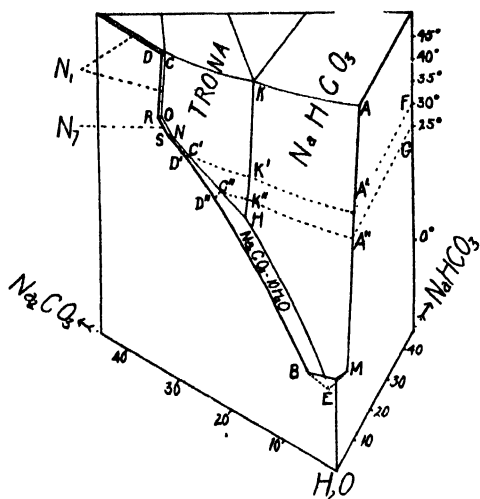


Fig. 4.—Space model of the system Na_2CO_3 - $\text{NaHCO}_3\cdot\text{H}_2\text{O}$.

M are the binary eutectics of Table I. The dotted lines $GA''K''C''D''$ and $FA'K'C'D'$ represent the temperatures of the isotherms at 25 and 30° , and the upper surface of the figure represents the isotherm at 50° .

Summary

1. Isotherms of the system: Na_2CO_3 - NaHCO_3 - H_2O at 25, 30 and 50° have been studied.

2. The double salt Trona, $\text{NaHCO}_3\cdot\text{NaCO}_3\cdot 2\text{H}_2\text{O}$, is stable in contact with saturated solutions from 21.26° , the temperature of its formation, up to at least 50° . It shows incongruent solubility throughout this entire range of temperatures. The range of concentrations within which it may be prepared increases gradually with increase in temperature. The salt forms a stable phase from solutions containing as little as 0.16%

⁹ Wells and McAdam (THIS JOURNAL, 29, 721 (1907)) found 32.00° at 31.34% and 35.37° at 33.19% as the two transition temperatures and concentrations.

of bicarbonate at 31.98° , and nowhere requires for its formation more than 3.74% of bicarbonate in the solution.

3. Four invariant temperatures for the ternary system have been found between the temperature of the ternary eutectic at -3.32 and 35.27° .

NEW YORK CITY

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. V. THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA BY RELATIVELY SHORT WAVE LENGTHS

BY LOUIS S. KASSEL AND W. ALBERT NOYES, JR.

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Very few photochemical studies in the far ultraviolet have been carried out. In a previous paper¹ a report was made of a study of the photochemical decomposition of anhydrous oxalic acid in the far ultraviolet. It was found, qualitatively, that the decomposition proceeded more rapidly with light transmitted by fluorite than with light transmitted by quartz.

The present work was undertaken with the object of determining the quantum efficiency of the decomposition of ammonia in the region of wave lengths below that transmitted by quartz.

I. Experimental Method and Results

It is possible to use fluorite windows for studies of the effects of radiations of slightly shorter wave lengths than those transmitted by quartz. Quartz may be said to transmit, under ideal conditions and in thin layers, as far as $185m\mu$. Fluorite is considerably more variable in its characteristics and the data on its transmission do not agree among themselves. Fluorite transmits relatively well to about $150m\mu$ and some authors report transmission as far as $100m\mu$.

Many authors have made spectroscopic investigations in the far ultraviolet. Methods of detection of the radiation were available which were far more sensitive than the ordinary methods which may be used in photochemical studies.

In the case of gas reactions, the rate of reaction can be determined by measurements of the pressure change. It is far more difficult to find a suitable light source, since the sources of light used by spectroscopists for studies in this region are usually too feeble to produce measurable photochemical effects unless the quantum efficiency of the reaction is high. In the present work two sources of light were tried. The first was a discharge tube of the type described by Hopfield.² This tube was used with both nitrogen and hydrogen, but the light emitted was found to be too feeble to produce

¹ Noyes and Kouperman, *THIS JOURNAL*, **45**, 1398 (1923).

² Hopfield, *Phys. Rev.*, **20**, 573 (1922).

measurable decomposition of the ammonia. The second type was a condensed discharge through hydrogen. The spark gap was of tungsten and the hydrogen was passed through in a continuous stream. The spark was brought about by means of a $\frac{1}{4}$ kilowatt transformer with a secondary voltage of approximately 8000 volts. A capacity of approximately 0.003 microfarad was used. The tube was cooled by a rapid stream of water and the sputtering was greatly reduced by the rapid flow of hydrogen.

In the preliminary experiments an attempt was made to measure the ammonia decomposition directly with a McLeod gage. This was found not to be feasible.

The procedure finally adopted was to freeze out the ammonia with liquid air and measure the residual pressure with a McLeod gage.³ The reaction chamber was 9 cm. in length and 2 cm. in diameter. The fluorite window was sealed on with a special vacuum wax and the bulb containing the spark gap was sealed directly to the other side of the window. There was, therefore, no air gap between the source of light and the reaction vessel.

The ammonia used in these experiments was a commercial product. On issuing from the cylinder it passed over sodium hydroxide and then over calcium oxide in order to remove most of the moisture. It was next condensed in a bulb surrounded by carbon dioxide snow and ether. After an appreciable amount had condensed, ammonia was drawn out of the system by a water pump until about 25% of it had disappeared. The system was then shut off from the water pump and the carbon dioxide snow and ether placed around a second bulb containing metallic sodium. After the ammonia had distilled over to the sodium the system was evacuated for a few minutes and the ammonia distilled onto a second quantity of sodium contained in a third bulb. The sodium dissolved in the ammonia to give a deep blue solution which was permanent until the ammonia was distilled off. The ammonia was finally distilled onto ammonium nitrate which had been dried for a period of several hours at a high vacuum and a temperature of 105°. The ammonia from this solution was used as needed.

In order to obtain the effect of radiation transmitted by fluorite but not by quartz, a quartz window was used in part of the experiments. The window was of clear crystalline quartz with a thickness of about 3 mm.

TABLE I
RATE OF DECOMPOSITION OF AMMONIA (WITH QUARTZ WINDOW)

Init. press. of NH ₃ , mm.	Init. residual press. mm. $\times 10^3$	Final residual press. mm. $\times 10^3$	Time, min.	dp/dt , mm. $\times 10^3$ /min.
240	1.423	8.208	406	0.01669
150	0.146	1.778	79	.02066
250	0.821	5.700	271	.01800
Average				.01845

Since the volume of the entire apparatus was 670 cc. and since one mole of ammonia gives two moles of decomposition products, the rate of decomposition of ammonia when quartz windows are used is found to be ($T = 25^\circ$) 3.32×10^{-10} moles per minute.

In order to calculate the quantum efficiency it is necessary next to determine the light intensity. Since the pressures used were relatively low and the fraction of the total intensity absorbed was small, it would be difficult to use the ordinary methods of determining light intensities.

³ The vapor pressure of solid ammonia has been measured by Karwat, *Z. physik. Chem.*, 112, 486 (1924). Extrapolation by means of his equation shows that at liquid-air temperatures the vapor pressure is less than 10^{-6} mm.

TABLE II
RATE OF DECOMPOSITION OF AMMONIA (WITH FLUORITE WINDOW)

Init. press. of NH ₃ , mm.	Init. residual press., mm. $\times 10^3$ ^a	Final residual press., mm. $\times 10^3$ ^a	Time, min.	dp/dt , mm. $\times 10^3$ /min.
185	2.043	10.62	188	0.04560
175	0.00	3.037	100	.03037
180	0.091	13.15	375	.03483
180	17.81 ^a	25.13	223	.03283
Average				.03591

^a In this experiment a quantity of air was purposely admitted. It seems to show that neither oxygen, nitrogen nor water vapor affects the decomposition markedly. Kuhn⁴ had previously shown that nitrogen and water vapor are without effect.

From the above data it is found that 6.470×10^{-10} moles of ammonia are decomposed per minute when fluorite windows are used.

Accordingly, a photochemical method was finally adopted. Warburg⁵ has determined the quantum efficiency for the formation of ozone from oxygen. Since oxygen absorbs in the same region as ammonia, it should be possible to obtain a good measure of the light intensity by means of this reaction.

Warburg⁵ finds that two molecules of ozone are formed per quantum absorbed. His values never quite attain this figure, but he used relatively high pressures and the quantum efficiency would approach two molecules per quantum at atmospheric pressure. From theoretical considerations, also, this value is probable.⁶ The mechanism may be pictured as a direct dissociation of oxygen with subsequent addition of the two atoms formed to normal molecules.

A calculation based on the data of Landsberg and Predwoditileff⁷ shows that for all wave lengths less than $214m\mu$ the absorption by ammonia is practically complete under the conditions of the experiments described. Few accurate quantitative data on the absorption of radiation by oxygen in this spectral region are available. Kreusler⁸ has determined the absorption coefficient of oxygen at two different wave lengths, $186m\mu$ and $193m\mu$. Bloch and Bloch⁹ have measured the wave lengths of many absorption lines of oxygen with a quartz spectrograph from 195.75 to $186.48m\mu$. Warburg⁵ at high pressures has obtained ozone at a wave length of $253m\mu$.

⁴ Kuhn, *Compt. rend.*, 177, 956 (1923); 178, 708 (1924); *J. chim. phys.*, 23, 521 (1926).

⁵ Warburg, *Sitzb. preuss. Akad. Wiss.*, 1914, 872; 1915, 230.

⁶ See Franck, *Trans. Faraday Soc.*, 21, 536 (1926); Born and Gerlach, *Z. Physik*, 5, 433 (1921); Hogness and Lunn, *Phys. Rev.*, 27, 737 (1926); Birge and Sponer, *ibid.*, 28, 259 (1926).

⁷ Landsberg and Predwoditileff, *Z. Physik*, 31, 544 (1925).

⁸ Kreusler, *Ann. Physik*, 6, 412 (1901); See Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923.

⁹ Bloch and Bloch, *Compt. rend.*, 158, 1161 (1914); *Le Radium*, 11, 99 (1914).

Recently, Hopfield and Leifson¹⁰ have studied the absorption spectrum of oxygen, using a layer 2.5 cm. in thickness at atmospheric pressure and the continuous spectrum of hydrogen as a background. They find sixteen clearly-resolved bands between 195 and 176m μ and a great absorption band from 175 to 130m μ . The conclusion may be drawn from the various lines of evidence mentioned that the absorption by oxygen under the conditions of these experiments would be very nearly complete for wave lengths below those transmitted by quartz and down to the limit of fluorite.

It would be possible, therefore, to determine the number of quanta emitted per second in this region of the spectrum by the source of light used in these experiments if oxygen could be passed through the reaction vessel and the amount of ozone formed determined. A similar calculation could not be made for the range of wave lengths transmitted by quartz, since the absorption bands of ammonia and of oxygen do not coincide.

Hydrogen shows only a faint continuous spectrum between 240 and 168m μ , since there is no many-lined spectrum in this region.¹¹ Since hydrogen at a pressure of one atmosphere begins to absorb strongly at 160m μ ,¹² the wave lengths transmitted by fluorite and not by quartz in these experiments lie mainly in the region between 190 and 160m μ . In addition, fluorite transmits slightly better than quartz for the wave lengths slightly longer than 190m μ . The effect of this on the results will be discussed later.

In order to determine the intensity of the light, an exit tube was sealed to the reaction chamber as close to the window as possible. Dry oxygen was streamed through the tube, entering at the back and leaving at the end near the light source.

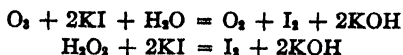
The quantity of ozone produced by the action of the light used was very small, so that it became necessary to devise a sensitive method for the determination of ozone. A colorimetric method was finally adopted. The oxygen issuing from the reaction vessel was led into a tube in such a manner that it came into contact with a piece of filter paper moistened with a solution of starch and potassium iodide. After the oxygen had streamed for a few minutes with the light on, the paper was observed to have become colored. The color, however, was brown instead of the blue usually associated with the starch-iodine complex. Several experiments were carried out with various oxidizing agents and it was finally found that solutions of hydrogen peroxide produced the same brown color. The equations for these reactions are as follows.¹³

¹⁰ Hopfield and Leifson, *Phys. Rev.*, 25, 716 (1925).

¹¹ Lyman, "The Spectroscopy of the Extreme Ultraviolet," Longmans, Green and Co., London, 1914, p. 75.

¹² Ref. 11, p. 71.

¹³ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922, Vol. I, p. 904, 940.



A number of starch-potassium iodide papers were prepared. To some of them a drop (weighed to within about 2%) of very dilute hydrogen peroxide was added. These served as standards. Others were exposed to the oxygen-ozone stream and the time which they required to develop a color that matched that of the standards was determined. Several sources of error might be mentioned. 1. The ozone formed might not be completely absorbed by the starch-potassium iodide papers. 2. The ozone might be partially decomposed by the ultraviolet light. The second of these errors is not serious.¹¹ However, both of these errors would produce an effect in the same direction, namely, the time of formation of the proper brown color would be increased. An idea of the error could be obtained by a variation of the rate of flow of the oxygen. Increase in the rate of flow produced no regular variation in the time required for a given darkening. The maximum variation was not over 20%, while the rate of flow was nearly tripled in some instances. In addition, two different concentrations of hydrogen peroxide were used, one three times the other, and the ratio of the average times for darkening is nearly the same as the reciprocal of the ratio of the concentrations.

The hydrogen peroxide solutions were made by diluting ordinary hydrogen peroxide to about 0.1 *N* and titrating with permanganate. This solution was subsequently diluted to 0.001591 *N* or 0.000530 *N*. In all of this work conductivity water was used. A fresh solution of hydrogen peroxide was prepared each day, although it was found that the solution could be kept fairly well in the dark. The oxygen was dried by phosphorus pentoxide before exposure to the light.

The weight of solution used was always 0.048 g., within about 2%. When the 0.001591 *N* solution was used with the fluorite window the average time for equivalent darkening was 30.10 minutes with a maximum deviation of 9.7%. With the 0.000530 *N* solution and fluorite window the average time was 10.07 minutes with a maximum deviation of 14.3%. With the 0.000530 *N* solution and the quartz window the average time was 36.21 minutes with a maximum deviation of 9.6%.

The ratio of the two concentrations used is 1:3.002, whereas the ratio of the average times is 2.989:1. One drop of the 0.000530 *N* solution is equivalent to 1.272×10^{-8} mole of ozone. The above figures give as a result, therefore, the production of 1.263×10^{-9} mole of ozone per minute when fluorite windows are used. A similar calculation with the more concentrated solution gives 1.268×10^{-9} mole per minute. For the quartz window it is found that 0.352×10^{-9} mole of ozone is formed per minute. The difference, or 9.14×10^{-10} , is the number of moles of ozone formed per minute by radiation transmitted by fluorite but not

by quartz. If the assumption is now made⁵ that two molecules of ozone are formed per quantum absorbed, it is found that 2.77×10^{14} quanta per minute are transmitted by fluorite in the region in which quartz does not transmit. Returning now to the photochemical decomposition of ammonia, it is found that 3.15×10^{-10} mole of ammonia is decomposed per minute by the radiation transmitted by fluorite but not by quartz. Multiplication by Avogadro's number (6.06×10^{23}) gives 1.91×10^{14} molecules of ammonia decomposed per minute. It is found, therefore, that on the average 0.690 molecule of ammonia is decomposed per quantum absorbed or, in other words, that 1.45 quanta are required on the average to decompose one molecule.

It is difficult to estimate the accuracy of this figure for the quantum efficiency. The determination of the quantity of ozone should not be in doubt by more than 10%. The values for the rate of decomposition of ammonia show good agreement with one exception. The actual numerical value may probably be written as 1.45 ± 0.50 quanta per molecule if the assumptions made in this work are justified. The assumption that both oxygen and ammonia absorb completely in the region between 190 and 160m μ seems to be justified on the basis of the best data available. The effect of the slightly better transmission of fluorite in the region between 190 and 220m μ would be to make the number of quanta absorbed per molecule too high rather than too low in the region under consideration.

II. Discussion of Results

The calculations made above are based on the assumption that the photochemical decomposition of ammonia proceeds according to the equation



This reaction has apparently been assumed by Warburg¹⁴ and by Kuhn.⁴ The former found that four quanta are absorbed per molecule decomposed in the spectral region 214–202.5m μ . The latter for the same spectral region found that 2.2 quanta are absorbed per molecule decomposed but that as the light became more nearly monochromatic (210–206.3m μ), about ten quanta were required on the average to make one molecule decompose.

More recently, Dickinson and Mitchell¹⁵ and Taylor and Bates¹⁶ have studied both the direct photochemical decomposition of ammonia and the decomposition sensitized by mercury vapor. No measurements of the quantum efficiency were made by either of these authors. There are some slight disagreements between the researches of these authors, but both are in agreement that more hydrogen is obtained in the non-condensable gases during the direct (unsensitized) photochemical de-

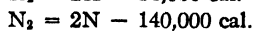
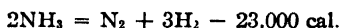
¹⁴ Warburg, *Sitzb. preuss. Akad. Wiss.*, 1911, 746; 1912, 216.

¹⁵ Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926); Mitchell and Dickinson, *THIS JOURNAL*, 49, 1478 (1927).

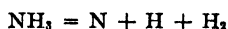
¹⁶ Taylor and Bates, *Proc. Nat. Acad. Sci.*, 12, 714 (1926).

composition than would be obtained if equation (1) were obeyed. This may indicate, perhaps, the formation of hydrazine. Taylor and Bates report that the non-condensable gases contain 96% of hydrogen, while Dickinson and Mitchell report 87% of hydrogen. Since Taylor and Bates used a dynamic method, while Dickinson and Mitchell used a static method, the discrepancy may be due to subsequent photochemical decomposition of hydrazine if it is left exposed to radiation. Since a static method was used in the experiments herein reported, and, in addition, a shorter wave length than that used by the other authors, the decomposition to nitrogen and hydrogen probably represents the majority of the reaction. In case hydrazine were formed, the number of molecules decomposed per quantum would be larger than that given above.

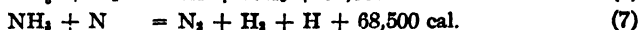
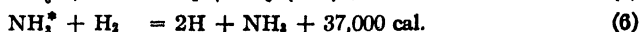
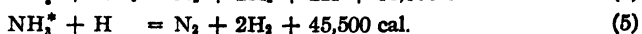
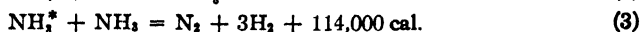
We may state, however, with a good deal of assurance that the quantum efficiency for the decomposition of ammonia is higher in the region 190–160m μ than it is in the region of the spectrum employed by Warburg¹⁴ and by Kuhn.⁴ Kuhn also reports that the quantum efficiency increases with the temperature and that at 500° only 0.3 quantum is absorbed per molecule decomposed. On the basis of the following heats of reaction



Kuhn has calculated that the dissociation

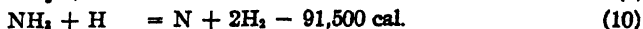
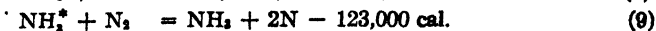


involves the absorption of about 124,000 calories. This corresponds to light of about 230m μ in wave length. Kuhn proposes a mechanism to account for the various observed facts. The criticism to which this mechanism is open is that the heats of dissociation used are probably too small. Witmer¹⁷ gives 100,000 calories per mole as the heat of dissociation of hydrogen obtained from an analysis of band spectra. Birge and Sponer⁶ give about 260,000 for nitrogen. While little confidence can be placed in mechanisms based on the sort of calculation referred to, it may be of interest to list those reactions which are possible and those which are not possible, using as a basis these more recent values for the heats of dissociation of hydrogen and of nitrogen. For a wave length of 208m μ , corresponding to 137,000 calories per mole, it is found that the following reactions are possible



¹⁷ Witmer, *Phys. Rev.*, **28**, 1221 (1926).

The following reactions are found to be impossible:



Any mechanism based on these figures would be somewhat different from that given by Kuhn. If there were no dissipation of energy, the resulting quantum efficiency would be 2, but this would not be expected in any actual case. Equation (6) is similar to that offered by Dickinson and Mitchell to explain the inhibiting effect of hydrogen on the sensitized decomposition of ammonia. Equation (9) would explain, similarly, the lack of effect of nitrogen. Kuhn offers similar explanations.

It may be of interest to point out the relation of the decomposition of ammonia to the ideas expressed by Franck.⁶ Ammonia in the gaseous state is doubtless made up almost entirely of non-polar molecules and the electron orbits of the molecule probably have little similarity to the electron orbits of nitrogen or hydrogen atoms. The heat of dissociation, as in the case of oxygen, would be high. Dissociation, as in oxygen, can follow the absorption of radiation only through the agency of collisions. In this case the probability of dissociation after collision would be a function of the electron energy levels at the time of collision, and the potential energy of the nuclear system would not vary greatly. Thus, we can see qualitatively that the shorter the wave length used, the greater the chance of dissociation. The apparent deviation from the Einstein Law of Photochemical Equivalence may be satisfactorily explained in this manner. One would expect that the quantum efficiency would approach unity at the point where continuous absorption begins. In line with the results herein reported, the quantum efficiency increases for short wave lengths and may be unity for the short wave lengths of the region studied.¹⁸

With regard to the nature of the particular dissociation process involved, we may offer only speculations since the band spectrum of ammonia has never been thoroughly analyzed. If the process involves the removal of one hydrogen, then two NH_2 groups might add to each other with the production of hydrazine. This would seem to be a most unlikely occurrence with low light intensities. If hydrazine is formed it would be more reasonable to explain it as a result of a collision of one NH_2 group with a normal ammonia with the resultant production of monatomic hydrogen and hydrazine. It seems somewhat more reasonable to expect that the collision between an excited ammonia molecule and a normal molecule would lead to a more profound decomposition with production of nitrogen and hydrogen.

¹⁸ See "Molecular Spectra in Gases," by Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Res. Council*, Vol. XI, Part 3, No. 57 (1926), for a full discussion of the relation of band spectra to dissociation.

Summary

1. The photochemical decomposition of ammonia by relatively short wave lengths has been studied. It is found that for the approximate region of the spectrum between 190 and 160 μ , 1.4 quanta are absorbed per molecule decomposed. This is based on the assumption that two molecules of ozone are produced from oxygen per quantum absorbed. The quantum efficiency is higher in this region of the spectrum than that found by other authors in the neighborhood of 210 μ .

2. A short theoretical discussion is given. It does not seem possible to give a mechanism for the reaction which is free from all criticism, but with the use of thermal data it is possible to indicate which reactions might be possible. The increase in quantum efficiency with increase in frequency of radiation receives a reasonable qualitative explanation on the basis of recent theories of band spectra.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 38]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER IV. KINETICS AT 100 AND 220°, THE TEMPERATURE COEFFICIENT BETWEEN 0 AND 220°, AND SUMMARY

BY ROBERT N. PEASE AND CARL A. HARRIS

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Previous work¹ on the hydrogenation of ethylene in the presence of copper has shown that at 0° the rate is increased by excess of hydrogen but decreased by excess of ethylene, while at 200° the rate indicates an approximation to a bimolecular reaction, in which case proportionate increases in rate are caused by excess of either hydrogen or ethylene. Obviously, at some intermediate temperature the reaction rate should be independent of the ethylene concentration and proportional to the hydrogen concentration alone. We have thought it worth while to investigate this case and at the same time to obtain additional data on the higher temperatures. Further, we have taken occasion to measure rates at a series of temperatures between 0 and 200° in order to obtain the conventional heat of activation of this reaction.

The apparatus and general method of procedure have been fully described in previous papers.^{1b} Suitable gas mixtures were made up in a calibrated gas buret and run into the evacuated catalyst chamber. The rate of reaction was then followed by the pressure decrease at constant volume.

¹ (a) Grassi, *Nuovo Cimento*, [6] 11, 147 (1916); (b) Pease, *THIS JOURNAL*, 45, 1198, 2235 (1923).

Two catalysts were used, one of which was partially deactivated by heating in order to carry out the measurements at intermediate temperatures. One of these catalysts consisted of approximately 10% by weight of copper on broken diatomite brick (kindly furnished by the Armstrong Cork Co.). The brick was sized to 4-10 mesh, thoroughly washed with nitric acid, dried and impregnated uniformly with the proper amount of copper nitrate solution. This solution was made up to such a concentration that its weight was approximately that of the brick, since the latter will take up its own weight of water without becoming distinctly wet. After slow drying, the catalyst was reduced in hydrogen at 200°. Sixty cc. of catalyst was used. The second catalyst was prepared by coating glass beads with metallic copper, precipitated from a warm alkaline solution of cuprous hydroxide with phenylhydrazine. The method is due to Chattaway,² and gives a uniform bright copper coating; 575 glass beads of average diameter 0.486 cm., possessing a total surface of 426 sq. cm., carried 0.409 g. of copper. The purpose of this type of catalyst was to get away from possible solution effects.

The brick-supported catalyst used in the present work did not prove as active as the bulk catalyst used earlier,³ and a comprehensive series of measurements at 0° was not attempted. The first such measurements were at 50°. As the disturbing effect of ethylene still persisted, the catalyst was partially deactivated by heating to 500° for eight hours in a vacuum. This treatment gave a catalyst of moderate activity at 100°.

Experiments at 100°.—The results of thirteen experiments at 100° are summarized in Table I. The initial rates were obtained by extra-

TABLE I
KINETICS AT 100°C.

Expt. No.	Ratio, H ₂ : C ₂ H ₄	Partial press., atm.		dp/dt mm./min.	$\frac{dp}{dt} \cdot \frac{1}{pH_2}$
		H ₂	C ₂ H ₄		$\frac{1}{\text{mm.}} \frac{1}{\text{atm.}}$
141	2:1	1/3	1/3	21.5	65
142	3:1	3/4	1/4	23.5	62
143	1:2	1/3	1/3	12.5	74
146	1:1	1/2	1/2	33.3	67
147	1:2	1/3	2/3	21.0	63
148	2:1	2/3	1/3	43.0	65
149	3:1	3/4	1/4	42.2	56
150	1:3	1/4	3/4	16.0	64
151	1:1	1/2	1/2	16.2	65
152	2:1	1/2	1/2	21.4	64
153	1:2	1/3	1/3	10.9	64
154	3:1	3/4	1/4	24.0	65
155	1:3	1/4	3/4	8.5	65

² Chattaway, *Chem. News*, 96, 85 (1907).

³ This is due, perhaps, to a smaller surface area.

polarization, and are compared with the initial partial pressures. The latter are calculated from the composition of the mixture and the initial pressure. The adsorptions of ethylene and hydrogen on this catalyst were not determined at 100°. At 50°, before deactivation, 0.15 cc. of hydrogen and 3.10 cc. of ethylene were adsorbed at 1 atm. and 0.15 cc. of hydrogen and 2.35 cc. of ethylene at $\frac{1}{2}$ atm. It is to be presumed that the deactivated catalyst would have adsorbed a negligible amount of hydrogen and something less than 1 cc. of ethylene at 100° and 1 atm. If adsorption were taken into account, the partial pressure of hydrogen would be increased and that of ethylene decreased slightly.

It is clear that over the range investigated the reaction rate is proportional to the hydrogen concentration alone, and the reaction is, therefore, monomolecular with respect to hydrogen and of zero order with respect to ethylene. This represents the transition from the behavior at low temperatures, when ethylene inhibits the reaction, to higher temperatures, when the reaction rate increases in proportion to the ethylene partial pressure.

Experiments at 220°.—In the original work at higher temperatures, the bulk copper catalyst was found to adsorb hydrogen very slowly. As it was thought that this might have interfered somewhat with the pressure measurements, new experiments have been carried out using as catalyst a film of copper deposited on glass beads. It was found that individual experiments gave very good bimolecular constants. Excess of ethylene, however, leads to an appreciably lower constant, as was found in the earlier work. Thus, the reaction is nearly but not quite normally bimolecular even at 220°. The average values of $K = (dp/dt)(1/p_{H_2} \cdot p_{C_2H_4})$ are given below; p is in millimeters of mercury, t is in minutes.

TABLE II
AVERAGE BIMOLECULAR CONSTANTS AT 220°

atm. H_2	Initial mixture atm. C_2H_4	$K \times 10^4$
$\frac{1}{2}$	$\frac{1}{2}$	1.8
$\frac{2}{3}$	$\frac{1}{3}$	2.0
$\frac{1}{3}$	$\frac{2}{3}$	1.75
$\frac{1}{4}$	$\frac{1}{4}$	1.9

The results are much the same as those previously obtained. The catalyst is about as active as a bulk copper catalyst deactivated at 500°.

Temperature Coefficient.—Runs were carried out with a 50% mixture, initially at 1 atmosphere, between 0 and 220°. From 0 to 60° the brick-supported catalyst before heat treatment was used; from 60 to 100° the brick-supported catalyst after heat treatment; from 194 to 220° the catalyst consisted of copper deposited on glass beads.

The question arises as to the basis upon which to compare rates at different temperatures, since the reaction kinetics change as the temper-

ature rises. A complete expression for the latter would take account of this. Full data on the rate at each temperature and on the small adsorptions would be required, however, and we have not thought it worth while to obtain these. Instead, we compare rates at equal pressures ($1/2$ atmosphere of each gas) and obtain therefrom the conventional heat of activation. The difference between this and the true heat of activation involves terms for the heats of adsorption.

The reaction velocity curves have been extrapolated back to 1 atmosphere initial pressure and the tangent taken at this point. The latter are taken as the velocity constants at each temperature. They are given in Table III along with values of A , the conventional heat of activation calculated from $\log \frac{k_2}{k_1} = \frac{A}{4.58} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$.

TABLE III		
HEATS OF ACTIVATION		
Brick-supported catalyst before deactivation		
Temp., °C.	dp/dt (1 atm.) = " k " (mm. per min.)	A , cal.
0	0.358	13,350
10	0.853	
20	2.32	
30	4.62	
40	9.21	
50	16.27	11,450
60	31.0	13,800
		Av. 13,400
Brick-supported catalyst after deactivation		
60	4.06	14,050
78.5	12.4	
100	34.1	12,300
		Av. 13,200
Copper film on glass beads		
194	14.6	6000
220	20.5	

It is clear that the conventional expression for temperature coefficient applies from 0 to 100°, and that deactivation of the brick-supported catalyst does not change the heat of activation. The lower value in the

194–220° range is characteristic of the reaction, not of the unusual catalyst. The data of Grassi^{1a} and of Pease^{1b} lead to the same result. Thus, Pease calculated the heat of activation to be 7000 cal. between 200 and 250°. Between 150 and 200° it was 10,800 cal. These values were obtained on the same sample of bulk copper catalyst in the same state of activation. Grassi's data give 12,000 cal. between 150 and 200°, and only 1300 cal. between 200 and 250°. Between 250 and 275° he found the temperature coefficient to be zero. A similar decrease in temperature coefficient is noticeable in the results of Morris and Reyerson on the hydrogenation of ethylene in presence of copper, platinum and palladium deposited on silica gel.⁴

Theoretical Interpretation.—In concluding for the present this work on the hydrogenation of ethylene in the presence of copper, it may be of interest to summarize it briefly and supply the interpretation based on Langmuir's theory of adsorption and surface catalysis.⁵

The Langmuir theory assumes that reaction takes place on the catalyst surface in a layer of adsorbed gas not more than one molecule deep. The reaction kinetics, therefore, depend on the adsorptions as these are affected by pressure and temperature changes.

Assuming, with Langmuir, the monomolecular film, assuming that every molecule striking bare surface condenses and that the amount adsorbed depends chiefly on the rate of evaporation, one obtains for the fraction, x , of surface covered: $x = k_1 p / (k_2 + k_1 p)$, where p is the pressure, k_1 is the rate of condensation on a free surface (and is practically equal to the number of impacts) and k_2 is the rate of evaporation from the completely covered surface. With small adsorptions, x is proportional to the pressure; with a nearly covered surface, x slowly approaches unity, and the fraction $(1 - x)$ of surface free of gas varies inversely as the pressure $(1 - x)p = k_2/k_1$. The adsorption changes with temperature on account of the variation of k_2 , the unit rate of evaporation, chiefly. The function is doubtless of the "vapor pressure" type, so that $d \ln k_2 / dt = Q/RT^2$, where Q is approximately the heat of adsorption.

Assuming k_1 independent of temperature (the square root of temperature is involved), this results, in the case that the adsorption is small ($x = k_1 p / k_2$), in x decreasing with the temperature in the same way that k_2 increases, pressure being constant. When the adsorption is large, so that $-(1 - x)p = k_2/k_1$, the fraction $(1 - x)$ of surface bare of gas increases with the temperature in the same way as k_2 increases, pressure being constant.

The above are the relations which we shall apply to the ethylene-hydrogen reaction. It is to be remembered that the fundamental equation

⁴ Morris and Reyerson, *J. Phys. Chem.*, **31**, 1224 (1927).

⁵ Langmuir, *THIS JOURNAL*, **38**, 2221 (1916).

expresses a limiting law. In particular, it assumes a uniform surface. Poisoning experiments with carbon monoxide,⁶ and other data indicate that this condition is very far from applying. Nevertheless, the "active" surface may be considered to be meant in this case.

We consider first the low temperature experiments. At 0° both ethylene and hydrogen are strongly adsorbed, the ethylene adsorption being the higher of the two. Ethane is loosely adsorbed only. The rate is approximately proportional to the hydrogen concentration and inversely as a fractional power of the ethylene concentration. We suppose that molecules of the two gases must be in favorable juxtaposition on the catalyst surface for reaction to occur, and that in view of the stronger adsorption of ethylene, the surface is largely covered with this gas. Then the fraction $(1 - x)$ of surface free of ethylene, and available for condensation of hydrogen, would be inversely proportional to the ethylene partial pressure. At a given partial pressure of ethylene, the chance that a hydrogen molecule will strike a vacant spot on the surface is proportional to its pressure. The resulting reaction would then take place at a rate proportional to the hydrogen pressure and inversely proportional to the ethylene partial pressure. The experimental results approximate to this sufficiently closely to warrant the conclusion that this expresses fairly accurately the actual condition. If reaction followed immediately on condensation of hydrogen on a vacant spot, the above relations should hold somewhat better. Actually there is probably some lag, so that at any moment there are both hydrogen and ethylene molecules on the surface, the effect being to complicate somewhat the relations of adsorptions to pressures.

In the simple case, the effect of temperature would be to increase the fraction $(1 - x)$ of surface free of ethylene, and to increase the rate in proportion to $(1 - x)$. The temperature coefficient of reaction would then be equal to that of k_2 , the unit rate of evaporation of ethylene from the surface. This assumes that the temperature coefficient of the surface reaction is zero, which is probably not the case. Actually the temperature coefficient probably includes as well a term for the surface reaction. In either case the rate should increase exponentially with temperature, as is found between 0 and 100°.

The preceding discussion covers one limiting case. At the other extreme, namely, at high temperatures with a very inactive catalyst and small adsorptions, there is to be expected a bimolecular reaction with a negative temperature coefficient. This follows from the conclusion that with small adsorptions the amount adsorbed (fraction of surface covered) will be proportional to the pressure ($x = k_1 p / k_2$). The chance that molecules of ethylene and hydrogen will be favorably situated for

⁶ Pease and Stewart, *THIS JOURNAL*, 47, 1235 (1925)

reaction is then proportional to the product of the pressures. With varying temperature and constant pressure, x will vary inversely as k_2 (the unit rate of evaporation) for each gas. Since k_2 increases with the temperature, x will decrease. At the highest temperatures, the surface reaction rate will become infinite, so that every time molecules of the two gases are suitably disposed on the catalyst surface, reaction will occur. The temperature coefficient of reaction will then be the product of the temperature coefficients of the unit rates of evaporation, and will be negative.

It was found that at 200 and 220° the reaction is in fact nearly bimolecular, and the temperature coefficient undoubtedly will be negative at about 300° and higher. At 250° it is practically zero. At 200° ethylene is still somewhat inhibiting the reaction, however, and this, together with a probable increase in the surface reaction rate with temperature in this range, accounts for the temperature coefficients being still positive.

The conditions at 100° correspond to a transition from low temperatures and large adsorptions, when ethylene inhibits, to high temperatures and small adsorptions, when ethylene behaves normally. Large ethylene adsorptions interfere with reaction by preventing condensation of hydrogen. Smaller ethylene adsorptions allow more hydrogen molecules to condense, but increase the possibility of a condensing hydrogen molecule finding no ethylene in proximity with which to react. The two effects seem to neutralize each other at 100° over the pressure range studied.

The characteristics of the ethylene-hydrogen reaction in the presence of copper closely duplicate those of the hydrogen-oxygen reaction in the presence of platinum, which has been thoroughly investigated by Langmuir.⁷ In the latter hydrogen inhibits the reaction at low temperatures and the temperature coefficient is positive. Stoichiometric relations and a negative temperature coefficient are observed at high temperatures. The kinetics are, therefore, much the same in the two cases.

Summary

1. It has been found that at 100° the hydrogenation of ethylene in the presence of copper takes place at a rate proportional to the hydrogen concentration and independent of the ethylene concentration over partial-pressure ranges of $1/8$ to $3/4$ atmospheres.
2. It has been shown that at 220° the reaction is nearly but not quite bimolecular.
3. Rates have been measured between 0 and 220° and heats of activation calculated. The normal expression has been shown to apply between 0 and 100°. At higher temperatures there is a marked decrease in temperature coefficient and in heat activation.

⁷ Langmuir, *Trans. Faraday Soc.*, 17, 621 (1922).

4. The results of these and earlier experiments on this reaction are summarized and interpreted.

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NOTE

Note on a Light Source for Continuous Spectrum.—Since the introduction of the photometric methods for the determination of the quantitative absorption of light by solutions, much difficulty has been experienced in finding a suitable light source. A Tesla spark under water fulfils most nearly the requirements but previous designs¹ of such lamps have not been satisfactory for general or continuous use.

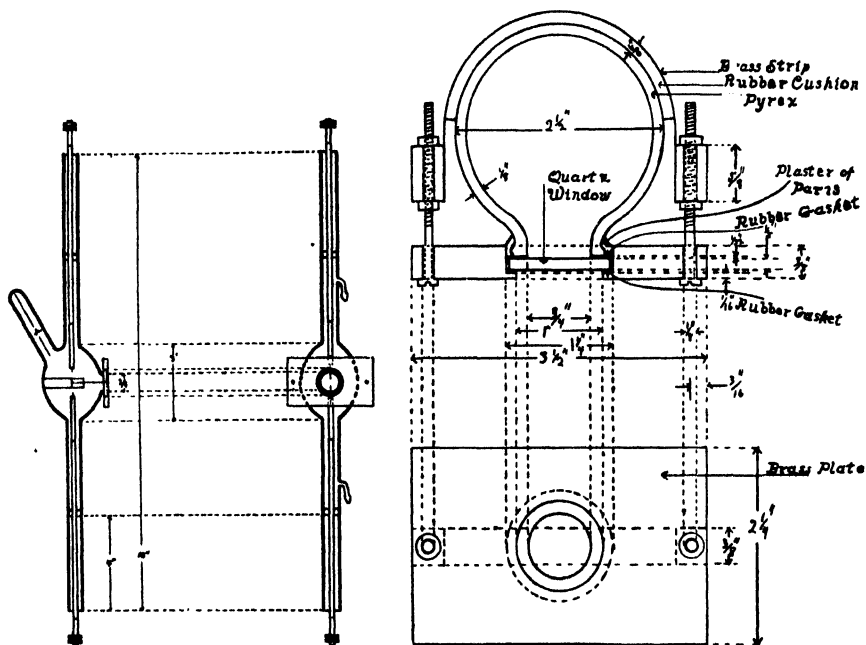


Fig. 1.—Continuous spectrum light source.

Fig. 2.—Continuous spectrum light source, detail of window clamp.

The accompanying cuts show the details of the completed lamp. Some points about its construction ought, however, to be mentioned. The glass sleeves carrying the brass rods are fire-polished until the inside diameter is slightly less than the diameter of the brass rod. The split end of the brass rod is then compressed and used to grind one end of the glass sleeve until the rod passes through to the other end where the grinding is continued. The two ground ends hold the brass rod rigidly in position.

¹ The most recent of these is described in the Bureau of Standards Scientific Papers, No. 440.

These prepared glass sleeves are placed on a 20-inch piece of the same brass rod and the whole is placed through the glass jacket of the lamp where the parts are held in position by a rubber stopper at each end. The plaster of Paris is then poured into the ends. After the plaster has set the long brass rod is replaced by the two split-end rods into which have been inserted the wires employed as electrodes. No. 16 drawn brass wire gave the best results.

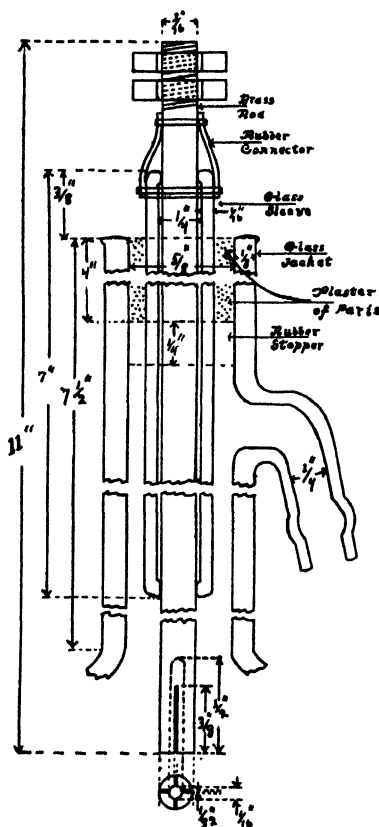


Fig. 3.—Continuous spectrum light source, detail of top end.

Earlier models of the lamp were made without a side tube, but without this cushion the bulb was frequently broken or the quartz window loosened. A lamp of this type has been in use in this Laboratory for three years.

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GERMANIUM. XVIII. FURTHER ORGANIC COMPOUNDS OF GERMANIUM¹

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Introduction

In previous papers² the authors have described the synthesis of some organic compounds of germanium. The study of these substances was undertaken not only to add to our knowledge of the rare element germanium, but also in the hope of being able to prepare organic compounds of either divalent or tetravalent germanium which would be soluble in water and which might be suitable for the treatment of pernicious anemia. It has been stated that an aqueous solution of germanium dioxide stimulates red cell formation³ but the value of the substance for this purpose appears to have been disproved by Bodansky.⁴

The present investigation was not carried as far as had been contemplated but, because of the withdrawal of two of us (W. R. O. and D. L. T.) from the field, it seems desirable to place on record such results as were obtained.

Experimental

Triphenyl Germanium Bromide, $(C_6H_5)_3GeBr$.—This compound was first prepared by Morgan and Drew⁵ by means of the Grignard reaction. Kraus and Foster⁶ describe the preparation of this substance by the bromination of tetraphenyl germanium by boiling a solution of the latter substance and bromine in carbon tetrachloride for several hours. Before their article appeared we had found that when ethylene dibromide is employed as a solvent only a few minutes' warming is required and that a perfectly pure product results after removal of the solvent and a single recrystallization from petroleum ether containing hydrogen bromide. The melting point of the substances was found to be 134° , a somewhat lower value than reported in the two papers mentioned above.

Anal. Subs., 0.2774, 0.2882. $AgBr$, 0.1352, 0.1410. Calcd. for $C_{18}H_{15}GeBr$: Br , 20.8. Found: 20.8, 20.8.

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

² (a) Tabern, Orndorff and Dennis, *THIS JOURNAL*, **47**, 2039 (1925); (b) Dennis, Orndorff and Tabern, *J. Phys. Chem.*, **30**, 1049 (1926).

³ (a) Hammett, Nowrey and Müller, *J. Exp. Med.*, **35**, 173 (1922); (b) Hammett and Nowrey, *ibid.*, 507; (c) Müller and Iszard, *Am. J. Med. Sci.*, **162**, 364 (1922).

⁴ Bodansky, *Proc. Soc. Exp. Biol. Med.*, **20**, 534, 536 (1923).

⁵ Morgan and Drew, *J. Chem. Soc.*, 127, 1760 (1925).

Kraus and Foster, *THIS JOURNAL*, **49**, 457 (1927).

Treatment of an alcoholic solution of the bromide with silver nitrate, filtration and dilution of the filtrate with water yielded triphenyl germanium oxide reported by Morgan and Drew.

Triphenyl Germanium Chloride, $(C_6H_5)_3GeCl$.—When triphenyl germanium oxide is dissolved in dry petroleum ether and the solution is saturated with hydrogen chloride, triphenyl germanium chloride separates in large, colorless crystals resembling the corresponding bromide. It may also be made by saturating a solution of triphenyl germanium bromide with hydrogen chloride and cooling. A third method consists in dissolving triphenyl germanium oxide in boiling alcohol and adding concentrated hydrochloric acid. The products prepared by each of these methods were recrystallized from petroleum ether and were found to melt sharply at 117–118°.

Anal. Subs., 0.1830: $AgCl$, 0.0765. Calcd. for $C_{18}H_{15}GeCl$: Cl , 10.5. Found: 10.3.

The Action of Two Moles of Bromine on Tetraphenyl Germanium.—The removal of two phenyl groups from tetraphenyl germanium was found to proceed much less smoothly than the removal of one, the evolution of some hydrogen bromide indicating the existence of side reactions. Since the direct isolation of diphenyl germanium dibromide was not found possible, subsequent reaction products were hydrolyzed directly. In addition to some triphenyl germanium oxide, two substances melting at 147 and 210° were formed. In all probability these were the complex dehydration products of diphenyl germanic acid previously reported by Morgan and Drew. As this reaction did not seem to offer a satisfactory way of preparing diphenyl germanium dibromide, it was not investigated further.

Unsymmetrical Aryl and Alkyl Germanes

Triphenyl *p*-Tolyl Germanium, $(C_6H_5)_3GeC_6H_4CH_3$.—Triphenyl *p*-tolyl germanium was prepared by the action of a large excess of *p*-tolyl magnesium bromide upon triphenyl germanium bromide. To insure the completion of the reaction, the ether was replaced by dry benzene, and the flask was heated to boiling for eight hours. The reaction mass was decomposed by a dilute aqueous solution of ammonium chloride and was subjected to prolonged steam distillation to remove all ditolyl. The product is best recrystallized from petroleum ether and alcohol or from glacial acetic acid; *m. p.* 123–124°.

Anal. Subs., 0.2238, 0.1781: CO_2 , 0.6209, 0.4960; H_2O , 0.1173, 0.0921. Subs., 0.2052, 0.2402: GeO_2 , 0.0553, 0.0650. Calcd. for $C_{24}H_{21}Ge$: C , 76.02; H , 5.62; Ge , 18.36. Found. C , 75.69, 75.98; H , 5.87, 5.75; Ge , 18.70, 18.78.

Triphenylanisyl Germanium, $CH_3OC_6H_4Ge(C_6H_5)_3$.—When treated in the same way, anisyl magnesium bromide (but not the iodide) and triphenyl germanium bromide yielded triphenylanisyl germanium. The product was finally recrystallized twice from alcohol and four times from glacial acetic acid, in both of which it is fairly insoluble in the cold. It melts at 158–159° (uncorr.).

Anal. Subs., 0.1758, 0.1845: CO_2 , 0.4720, 0.4945; H_2O , 0.0888, 0.0933. Subs., 0.2150, 0.1973: GeO_2 , 0.0543, 0.0505. Calcd. for $C_{24}H_{21}OGe$: C , 73.02; H , 5.40; Ge , 17.68. Found: C , 73.24, 73.12; H , 5.65, 5.66; Ge , 17.53, 17.77.

Triphenylethyl Germanium, $(C_6H_5)_3GeC_2H_5$.—Triphenylethyl germanium was prepared, in good yield, in essentially the same manner from triphenyl germanium bromide and ethyl magnesium bromide; m. p. 75–76°.

Anal. Subs., 0.2254, 0.2130: CO_2 , 0.5938, 0.5612; H_2O , 0.1239, 0.1122. Subs., 0.1812, 0.3982, 0.1493; GeO_2 , 0.0571, 0.1251, 0.0465. Calcd. for $C_{20}H_{20}Ge$: C, 72.12; H, 6.06; Ge, 21.82. Found: C, 71.87, 71.86, H, 6.15, 5.89; Ge, 21.86, 21.81, 21.62.

Triphenyldimethylanilino Germanium, $(CH_3)_2NC_6H_4Ge(C_6H_5)_3$.—Specimens of triphenyl germanium bromide were refluxed with an excess of dry dimethylaniline under varying conditions but no interaction took place.

One mole of triphenyl germanium bromide and two moles of *p*-bromodimethylaniline were dissolved in xylene and the liquid was refluxed with an excess of sodium. Sodium bromide separated and after an hour the metal retained its fresh surface. The solvent was decanted and as much of it as possible removed under moderate diminished pressure. The addition of alcohol resulted in the separation of slightly brownish, crystalline nodules. After recrystallization from hot petroleum ether and alcohol the product melted at 138–140°. Purified through the hydrochloride, it melted at 140–141° and still retained a brownish tinge.

Anal. Subs., 0.2004, 0.1891: CO_2 , 0.5423, 0.5117; H_2O , 0.1074, 0.1037. Subs., 0.2137, 0.2136: GeO_2 , 0.0527, 0.0525. Calcd. for $C_{28}H_{28}NGe$: C, 73.64; H, 5.95; Ge, 17.11. Found: C, 73.82, 73.82; H, 5.997, 6.137; Ge, 17.12, 17.06.

Passage of hydrogen chloride through an ethereal solution of triphenyldimethylanilino germanium yields at once the solid, crystalline hydrochloride, which may be separated either by evaporation of the ether or by decantation. It is insoluble in water and in hydrochloric acid, but dissolves readily in absolute alcohol, from which it is precipitated by the addition of water. It melts with decomposition between 105 and 110°. From it pure triphenyldimethylanilino germanium may be secured by treatment with alkali.

Tetrabenzyl Germanium and Its Tetrasulfonic Acid

Tetrabenzyl Germanium, $(C_6H_5CH_2)_4Ge$.—Nine g. of magnesium turnings was suspended in ether and the formation of the Grignard reagent was initiated by the addition of about 5 g. of benzyl chloride. A mixture of 40 g. of benzyl chloride, 10 g. of germanium tetrachloride and five volumes of dry xylene was then added drop by drop with good mechanical stirring and gentle refluxing. Finally, sufficient xylene was added to form a thin paste and the ether was distilled off on a steam-bath. Heating on the steam-bath was continued for some hours and the mixture was allowed to stand for two days. On working it up in the usual manner, taking care to subject the organic product to a vigorous and prolonged steam distillation to insure the removal of all dibenzyl, a nearly quantitative yield of tetrabenzyl germanium was secured. The first product melted at 106–107°, and at 107–108° after repeated crystallization from several solvents, including alcohol and petroleum ether.

Anal. Subs., 0.2116, 0.2000: CO_2 , 0.5991, 0.5660; H_2O , 0.1236, 0.1182. Subs., 0.2007, 0.1923: GeO_2 , 0.0481, 0.0466. Calcd. for $C_{24}H_{20}Ge$: C, 76.92; H, 6.46; Ge, 16.62. Found: C, 77.24, 77.10; H, 6.54, 6.61; Ge, 16.64, 16.82.

Tetrabenzyl Germanium Tetrasulfonic Acid, $(SO_3HC_6H_4CH_2)_4Ge$.—The above germane is preferably sulfonated by slowly dissolving it in an excess of 25% fuming sulfuric acid, keeping the temperature below 35°. Rapid agitation is essential. After standing for half an hour at room temperature, the reaction mixture was poured upon ice and the excess of sulfuric acid was removed by barium carbonate. When alcohol was added to the decolorized and strongly concentrated filtrate, the barium salt separated as an oil which changed to a white, crystalline solid on the addition of more al-

cohol. The solid was ground in a mortar with anhydrous acetone and was dried, first at room temperature and then at 110°. This substance, the normal barium salt of tetrabenzyl germanium tetrasulfonic acid, dissolves readily and completely in cold water, but is insoluble in acetone, alcohol or ether.

For analysis for either barium or sulfur alone the sample was decomposed by fusion in a nickel crucible with a mixture of potassium hydroxide and potassium nitrate. Germanium was determined in other samples by dissolving them in boiling water and precipitating the barium by the addition of an excess of sulfuric acid. The filtrate was concentrated and finally heated to 120° in a platinum crucible. Fuming nitric acid was added and the determination of germanium was carried out as described by Tabern, Orndorff and Dennis.^{2a}

Anal. Subs., 0.3615, 0.3730: BaSO₄, 0.1640, 0.1690. Subs., 0.2899, 0.3874: BaSO₄, 0.2618, 0.3442. Calcd. for C₂₀H₂₄Si₄O₁₂Ba₂Ge: Ba, 26.75; S, 12.46; Ge, 7.06. Found: Ba, 26.62, 26.66; S, 12.40, 12.20.

Anal. Subs., 0.5433, 0.6897: BaSO₄, 0.2505, 0.3156; GeO₂, 0.0562, 0.0706. Found: Ba, 27.15, 26.92; Ge, 7.18, 7.10.

Simple and Substituted Germanic Acid Anhydrides

Phenyl Germanic Acid Anhydride, (C₆H₅GeO)₂O.—One mole (3.6 g.) of mercury diphenyl and one mole (2.1 g.) of germanium tetrachloride were dissolved in dry xylene and heated at 140° in a sealed Pyrex bulb for two days. The contents of the bulb was diluted with absolute ether and filtered. The solid residue was pure phenyl mercuric chloride. The filtrate was further diluted with benzene and was treated with water containing a few drops of ammonium hydroxide. On standing, a granular precipitate separated at the liquid interface. This was filtered off and dried at 115°. Although quite pure, the substance was dissolved in dilute sodium hydroxide and was precipitated hot by neutralization of the solution with acetic acid.

Anal. Subs., (A) 0.2149, (B) 0.1885: GeO₂, 0.1302, 0.1140. Calcd. for C₆H₅-GeOOH: Ge, 39.7; for C₁₂H₁₀O₂Ge₂: Ge, 41.8. Found: 41.9, 41.9.

These analytical results indicate that the product in hand approached quite closely to the anhydride in composition, though Morgan and Drew concluded that the acid secured by them in small amount as the end fraction from a Grignard reaction was the fully hydrated form.

The anhydride of phenyl germanic acid is a white, fluffy, amorphous solid, insoluble in water and organic solvents, but soluble in excess of alkali; from such solution it is precipitated in lustrous flakes by carbon dioxide. It has no definite melting point.

***p*-Tolyl Germanic Acid Anhydride, (CH₃C₆H₄GeO)₂O.**—Mercury ditolyl and germanium tetrachloride when heated at 160–190° in xylene yielded *p*-tolyl germanic acid anhydride. The method of isolation was essentially the same as in the preceding instance.

Anal. Subs., 0.2100, 0.2309: GeO₂, 0.1175, 0.1285. Calcd. for C₇H₇GeOOH: Ge, 36.9; for C₁₄H₁₄O₂Ge₂: Ge, 38.65. Found: Ge, 38.9, 38.6.

Benzyl Germanic Acid Anhydride, (C₆H₅CH₂GeO)₂O.—Equimolecular quantities of mercury dibenzyl and germanium tetrachloride (4.2 g.) were dissolved in xylene and heated in a closed tube between 115 and 120° for two days. A higher temperature results in the decomposition of the mercury dibenzyl. The isolation of the benzyl germanic acid anhydride was carried out as in the case of the phenyl analog except that

here, because of the marked solubility of the benzyl mercuric chloride, water was added directly to the xylene solution without filtration.

Benzyl germanic acid anhydride is a colorless, granular precipitate, soluble in alkalies, fairly soluble in boiling water and in pyridine, but insoluble in organic solvents.

Anal. Subs., 0.1958, 0.1269: GeO_2 , 0.1074, 0.0690. Calcd. for $\text{C}_7\text{H}_7\text{GeOOH}$: Ge, 36.9; for $\text{C}_{14}\text{H}_{14}\text{Ge}_2\text{O}_4$: Ge, 38.65. Found: Ge, 38.1, 37.7.

Dimethylaminophenyl Germanic Acid Anhydride, $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{GeO}]_2\text{O}$.—Ten grams of germanium tetrachloride and an excess of dry dimethylaniline were placed in a flask which was then sealed and heated to 100 – 110° for two days. The strongly fluorescent gelatinous product was made alkaline and was subjected to steam distillation. After filtration carbon dioxide was passed into the resultant clear solution until the acid anhydride was completely precipitated. Re-solution and reprecipitation were repeated until the filtrate contained no germanium dioxide. The product may also be purified by dissolving it in acid and precipitating it with dilute ammonium hydroxide.

Dimethylaminophenyl germanic acid anhydride is a pearly white, fluffy powder, soluble in very dilute mineral acids, and also in an excess of alkali. Like the preceding anhydrides it does not have a definite melting point.

Anal. Subs., 0.1896, 0.2581: CO_2 , 0.3043, 0.4174; H_2O , 0.0825, 0.1134. Subs., 0.2068, 0.1985: GeO_2 , 0.1006, 0.0955. Calcd. for $\text{C}_8\text{H}_{11}\text{O}_2\text{NGe}$: C, 42.53; H, 4.9; Ge, 32.17. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_2\text{Ge}_2$: C, 44.30; H, 4.65; Ge, 33.50. Found: C, 43.78, 44.12; H, 4.88, 4.92; Ge, 33.76, 33.40.

When a thin layer of the above anhydride is kept for some time in an atmosphere of dry hydrogen chloride, it is converted entirely into the hydrochloride of dimethylanilino germanium trichloride; $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{GeO}]_2\text{O} + 8\text{HCl} = 2\text{HCl}(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{GeCl}_3 + 3\text{H}_2\text{O}$. The above hydrochloride melts with decomposition near 110° . It is readily and completely soluble in water and from such a solution ammonium hydroxide precipitates dimethylaminophenyl germanic acid anhydride.

Tetra-*n*-butyl Germanium, $(\text{C}_4\text{H}_9)_4\text{Ge}$.—Germanium tetrachloride was added to a large excess of butyl magnesium bromide, the reaction being carried out essentially in the manner described in a previous paper for the propyl analog. The desired product was thus secured in good yield as an almost odorless, oily liquid boiling between 178 and 180° at 733 mm. Unlike its lower homologs, it is ignited only with difficulty.

Anal. Subs., 0.2648, 0.1986: CO_2 , 0.6178, 0.4590; H_2O , 0.2855, 0.2081. Subs., 0.2384, 0.2415: GeO_2 , 0.0826, 0.0829. Calcd. for $\text{C}_{16}\text{H}_{36}\text{Ge}$: C, 63.81; H, 12.06; Ge, 24.13. Found: C, 63.65, 63.03; H, 12.07, 11.72; Ge, 24.05, 23.83.

Summary

A further study of the organic compounds of germanium—especially those containing potential solubilizing groups—has led to the synthesis and study of the following types of substances: (1) triphenyl germanium halides; (2) mixed aryl and alkyl derivatives, with and without a salt-forming group; (3) tetrabenzyl germanium and its tetrasulfonic acid; (4) simple and substituted phenyl germanic acid anhydrides; (5) tetra-*n*-butyl germanium.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

AFFINITY, REACTIVITY AND STRUCTURE IN ACETAL FORMATION. II

BY WALTER H. HARTUNG AND HOMER ADKINS

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The investigation of the relationship between the structure of various alcohols and aldehydes and the rate and extent of the reversible reaction $RCHO + 2R'OH \rightleftharpoons RCH(OR')_2 + H_2O$ has been continued.¹ It has been often assumed that the effect of a given substituent upon the equilibrium point was qualitatively if not quantitatively constant. There would then be certain groups that might be described as "positive" and others as "negative." It has now become evident that this is by no means true. A methyl group, for example, may in one case increase affinity and in another decrease the affinity for the same type of reaction. A methyl group may be more "negative" than a phenyl, a bromine more "positive" than a hydrogen and an hydroxyl more "negative" than a bromine.

This is a result to be expected if the effect of a group in lowering or increasing affinity is considered to be the result of a shift of the electronic structure. The shift resulting from the introduction of a substituent into a compound will depend not only on the character of the substituent but upon the character of the substituted compound, that is, upon the particular electronic system that is acted upon. The *effect* of the shift upon affinity will be dependent upon a third factor, that is, upon whether the shift has produced an electronic configuration which requires *more or less* energy to get the electrons (that is, their orbits) into a position where a new linkage may be formed with the particular reactant involved. It appears that a given substituent does not bring about simply a dislocation of electron pairs towards or away from the reactive end of the molecule but that it modifies the whole electronic architecture of the molecule. It is evident that the positivity or negativity of a group may not be defined except for the reactions of specific compounds.

The experimental results are summarized in Table I. For the sake of convenience the aldehydes are regarded as beta substitution products of acetaldehyde, a quantitative measure of the effect of the substituent being given in the third column of the table under $-RT \ln K_e$. The value of the expression $-RT \ln K$ would be that of the decrease in free energy ΔF if the activities of the reactants were equivalent to the analytically determined concentrations. Since for the present the activities are not known, it seems preferable not to consider the decrease in free energy to be equal to the values of $-RT \ln K$ but to refer to them as "affinity

¹ Adkins and Adams, *THIS JOURNAL*, 47, 1368 (1925).

values." It is possible that the absolute values of $-RT \ln K$ are of little significance,² and that even the relative values vary in different solvents.

The equilibrium point was approached from both sides in the case of aldehydes 4, 5, 7, 8, 12 and 15. The data for aldehydes 1, 2, 3, 6, 10, 11, 12 and 15 have not been previously published. Data on aldehydes 4, 5, 7, 8 and 14 were published by Adams and Adkins but the experimental work has been repeated and corrected values are given here. The new values are of the same order as those previously published except in the case of heptaldehyde. The equilibrium constants for aldehydes 9 and 13 were recalculated from Adams' data and are given here for the sake of ready comparison. Aldehydes 1, 2, 3, 6, 10 and 11 have never been prepared in a state of purity so that the equilibrium could not be obtained from the synthetic side.

TABLE I

EFFECT OF BETA SUBSTITUTION IN ACETALDEHYDE UPON AFFINITY IN ACETAL FORMATION

No.	Aldehyde	β -substituent	K	$-RT \ln K$
1.	Amino-acetaldehyde	$\text{NH}_2\text{HCl}-$	0.1340	1190 \pm 200
2.	Bromo-acetaldehyde	$\text{Br}-$.1121	1300 \pm 200
3.	Cyano-acetaldehyde	$\text{CN}-$.1070	1320 \pm 200
4.	Heptaldehyde	$\text{C}_6\text{H}_{11}-$.0970	1380 \pm 30
5.	Propionaldehyde	CH_3-	.0782	1510 \pm 30
6.	Imino-acetaldehyde	$-\text{NH}(\text{HCl})-$.0770 ^a	1520 \pm 200
7.	Acetaldehyde	$\text{H}-$.0744 ^b	1540 \pm 30
8.	Butyraldehyde	C_2H_5-	.0691	1580 \pm 30
9.	<i>iso</i> Butyraldehyde	$(\text{CH}_3)_2$.0355	1980 \pm 30
10.	β -Chloropropion-aldehyde	$\text{CH}_2\text{Cl}-$.0294	2090 \pm 200
11.	Glycolic aldehyde	$\text{HO}-$.0202	2300 \pm 200
12.	Acrolein	$\text{CH}_2=$.00455	3270 \pm 30
13.	Benzaldehyde00163	3810 \pm 30
14.	Cinnamaldehyde	$\text{C}_6\text{H}_5\text{CH}=$.00089	4160 \pm 30
15.	Crotonaldehyde	$\text{CH}_3\text{CH}=$.00063	4360 \pm 30

^a The calculations are based on the assumption of the hydrolysis of both acetal groups.

^b The authors are indebted to A. E. Broderick for the value for diethyl acetal and for other valuable assistance.

The equilibrium points for these six aldehydes were determined by the colorimetric method so that the values for $RT \ln K$ should be read ≈ 200 . The analytical method used for the determination of the other aldehydes should give a value accurate to within ≈ 30 units.

From an inspection of the table it becomes evident that the normal chain aliphatic aldehydes (Nos. 4, 5, 7 and 8) occupy, within a relatively narrow range, nearly the same position and are very high in the scale, whereas *isobutyraldehyde* (No. 9), with a branched chain, is decidedly lower. The hydrochloride of amino-acetaldehyde shows a high affinity

² See Conant, *THIS JOURNAL*, 49, 293 (1927).

value, as would be expected from the positive nature of the amino group. Bromo-acetaldehyde and cyano-acetaldehyde are practically alike as one would expect but that both should show a slightly greater affinity than acetaldehyde is indeed striking, for both the bromo and cyano groups are commonly considered negative and one would, therefore, expect them to have a marked depressing effect. Glycolic aldehyde, on the other hand, shows a marked lowering of affinity as compared with acetaldehyde. While a halogen on the alpha carbon of acetaldehyde is "positive" in its effect, the same is not true of beta-halogenated propionaldehyde, for β -chloropropionaldehyde is decidedly lower in affinity than is propionaldehyde. These results seem to conflict with those obtained by Wegscheider³ and Derick⁴ who studied the effect of halogen substitution on the dissociation constants of saturated aliphatic acids.

In 2,3 unsaturated aldehydes the affinity is much lower than in the saturated aldehydes. Acrolein drops almost to the level of benzaldehyde, and if a methyl or phenyl group is substituted for hydrogen on the beta carbon of acrolein a further lowering in affinity is observed, the alkyl having an even greater effect than the aryl group. That the phenyl group should exercise such influence is not surprising when one compares the relative positions of acetaldehyde and benzaldehyde; but the affinity value for crotonaldehyde indicates that the effect of a methyl in an unsaturated aldehyde is very different from that in a saturated one.

Experimental Method

In general the procedure of Adams was followed, known amounts of reactants being mixed in a dry Pyrex test-tube of suitable size and the tube closed with a stopper bearing a sampling device. The latter was made by sealing a 5cc. pipet to the single arm of a three-way stopcock. One of the double arms was extended to reach the bottom of the reaction tube while the other was lengthened and bent to permit exactly 5 cc. of the solution to be delivered into a suitable receiver. The concentration of the catalyst in the synthetic reactions was usually that used by Adams, while in the slower hydrolytic reactions the concentration was five or ten times as great. The reactions were allowed to proceed at 25°. In those cases where the aldehyde was available both the synthetic and hydrolytic reaction were carried out. In the other cases the hydrolysis was carried out at two different concentrations.

Preparation and Purification of Materials

Ethyl alcohol, acetaldehyde and ethyl acetal were purified as described in previous papers.⁵ The ethyl acetals of propionaldehyde, butyraldehyde and heptaldehyde were

³ Wegscheider, *Monatsh.*, **23**, 289 (1902).

⁴ Derick, *THIS JOURNAL*, **33**, 1152 (1911).

⁵ (a) Child and Adkins, *ibid.*, **45**, 3013 (1922). (b) Adkins and Nissen, *ibid.*, **44**, 2749 (1922).

prepared by Nissen's method. The diethylpropional had a density (referred to water at 4°) of 0.8232, and the diethylbutyral, of 0.8417 at 25°. Butyraldehyde was purified through the bisulfite compound, the vapors being dried over calcium chloride as in the purification of acetaldehyde and finally fractionated under reduced pressure. It boiled below 12.5° at 60 to 80 mm. Its density at 25° was 0.7988 and its refractive index (Abbé) at 25° was 1.3750. The propionaldehyde boiled 46.5 to 47.4° at 740 mm. The cinnamic aldehyde boiled at 108–109° at 35 mm. Its density at 25° was 1.045. Heptaldehyde was purified through the bisulfite addition compound and by the hydrolysis of diethylheptal. The final step in purification was a distillation carried out so slowly at 30–34° at 4 mm. that there was no noticeable ebullition. The density at 25° was 0.815 and the refractive index (Abbé) at 25° was 1.4077.

The Diethyl Acetal of Bromo-acetaldehyde was prepared by a modification of the method of Pinner⁶ and Fischer.⁷ One mole of bromine was added from a dropping funnel, during 30 to 45 minutes, to a well agitated mixture of one mole of diethyl acetal and 55 g. of precipitated calcium carbonate. The reaction mixture was kept in an ice-bath but the bromination proceeded best if the temperature was allowed to rise as much as possible without allowing the loss of the acetal, namely, to about 10°. The mixture was allowed to stand for 8 to 24 hours and enough steam introduced to dissolve the salts. The crude oil was then separated and placed over potassium carbonate. The aqueous layers from several brominations were steam distilled and the acetal so obtained was added to the crude oil, which was then washed with potassium carbonate solution until free from acid and dried for at least 12 hours over fresh potassium carbonate. The product was then fractionated. From 246 to 332 g. of the bromo-acetal boiling at 167–170° was obtained from 472 g. (4 moles) of acetal. This slightly colored product may be purified by distilling at 3 mm. pressure, shaking for 45 minutes with granular potassium carbonate and distilling at 48–49° (3 mm.). The density at 25° is 1.28. The pure acetal after a few hours becomes colored, and black after several days. The crude acetal, that is, the material boiling at 167–170°, was kept for months with little loss. It is a powerful lachrymator.

The Cyano-acetal was prepared by a modification of the method of Wohl.⁸ One hundred and thirty-two g. of bromo-acetal, 86.5 g. of potassium cyanide, 11 g. of potassium iodide, 300 cc. of alcohol and 150 cc. of water were gently refluxed for 72 hours in an oil-bath. The reaction mixture was steam distilled, the first portions of the distillate being diluted with water to throw out the acetal. After drying over granular potassium carbonate the crude product was fractionated at 5 mm. pressure, the compound boiling at 52–54°. At 15 mm. the boiling point is 55–57°; higher pressures result in considerable decomposition. The water-white acetal, density 1.255 at 24°, remains colorless if sealed in glass but becomes colored if allowed to stand in air. Such colored acetal should be allowed to stand with potassium hydroxide for an hour and be re-distilled at 5 mm. pressure.

The Acetal of Glycolic Aldehyde was prepared by a modification of the method of Pinner.⁶ A mixture of 66 g. of bromo-acetal, 37 g. of potassium hydroxide and 300 cc. of 95% alcohol was gently refluxed for 72 hours. The alcohol was distilled and the residue shaken with water. The oily layer was separated and the water layer extracted with ether. The oily layer was added to the ether and the whole dried over potassium hydroxide for 12 hours. The product was fractionated, that portion boiling at 163–167° being the desired product. This was fractionated at 8 mm., boiling at 57–58°; or 49–51° at 3–4 mm. The yields were from 40 to 60% and the density at 24° was 0.888.

⁶ Pinner, *Ber.*, 5, 149 (1872).

⁷ Fischer, *Ber.*, 25, 2551 (1892).

⁸ Wohl, *Ber.*, 39, 1952 (1906).

Acetal Amine (Amino Acetal) and Diacetal Amine were obtained by a modification of the method of Wohl⁹ and Wolff.¹⁰ Absolute ethanol was saturated at 0° with anhydrous ammonia and for each 7 g. of alcoholic ammonia 1 g. of bromo-acetal was used. The mixture was then sealed in tubes and heated at the temperature of boiling toluene for 18-24 hours. Any solid that may have formed was filtered off and the alcohol distilled from the filtrate. The residue from the distillation and the solid first obtained were combined, taken up in water and treated with alkali, whereupon an insoluble layer collected on the surface of the liquid. This was drawn off, the aqueous layer extracted several times with ether, the ethereal extract and the product first obtained were combined and dried over solid potassium hydroxide for at least 12 hours. The ether was distilled off and the residue repeatedly fractionated under reduced pressures. Fractions boiling at 52-53° at 2 mm. and at 127-130° at 3 mm. were obtained. The compound of lower boiling point had a density at 25° of 0.9161 and a refractive index (Abbé) of 1.4120. Analysis for nitrogen by combustion showed:

Anal. Calcd. for $\text{H}_2\text{NCH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$: N, 10.52. Found: 10.88.

The compound of higher boiling point had a density of 0.9541 at 25° and a refractive index of 1.4210.

Anal. Calcd. for $\text{HN}(\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)_2)_2$: N, 5.62. Found: 5.96.

Crotonic Aldehyde was prepared from aldol by slowly distilling it at ordinary pressures through a 30cm. Vigreux fractionating column. The unsaturated aldehyde was obtained from the distillate by salting out with calcium chloride, drying and redistilling at ordinary pressures; b. p., 101-104°.

Acrolein.—The method used for the preparation of acrolein has been described by us in "Organic Syntheses."¹¹ The product boiled at 52.5 to 53.5° and had a density at 0° of 0.859 and at 25° of 0.8377.

The Acetals of Acrolein and Crotonic Aldehyde and the Acetal of β -Chloropropionaldehyde were prepared by the method of Witzemann¹² and of Evans and Hass.¹³ The acetal of β -chloropropionaldehyde, having a boiling point at 3-4 mm. of 47-50° and a density of 0.983 at 25°, was obtained in a yield of 41%. The β -chlorobutyraldehyde acetal used as an intermediate in the preparation of the acetal of crotonic aldehyde boiled at 70-90° at 40-45 mm. pressure. The acetal of crotonic aldehyde boiled at 146-148° at 740 mm. and at 33-34° at 2.5 mm. The yields of the acetal on the basis of crotonaldehyde used were only 4-7%. The density of crotonic aldehyde acetal at 25° was 0.846.

Analytical Determination of the Concentration of Reactants at the Equilibrium Point.—The concentrations at equilibrium of acetaldehyde, heptaldehyde, butyraldehyde, propionaldehyde, cinnamic aldehyde and crotonic aldehyde were determined by the modified Seyewitz-Bardin method as described in previous papers. Numerous titrations of weighed amounts of the purified aldehydes showed that under the conditions present in the titrations one mole of butyraldehyde reacted with 0.95 mole of bisulfite, one mole of heptaldehyde with 0.90 mole of bisulfite, one mole of crotonic aldehyde with 1.85 moles of bisulfite and one mole of cinnamic aldehyde

⁹ Wohl, *Ber.*, 21, 617 (1888).

¹⁰ Wolff, *Ber.*, 21, 1481 (1888).

¹¹ "Organic Syntheses," 6, 1, John Wiley and Sons, Inc., New York City, 1926.

¹² Witzemann, *This Journal*, 36, 1909 (1914).

¹³ Evans and Hass, *ibid.*, 48, 2703 (1926).

hyde with 1.84 moles of bisulfite. It was demonstrated that the alkene linkage, in the acetals of the two last-mentioned aldehydes, did not react with the sulfite under the conditions of titration. The above values were used in calculating from the titration values the amounts of the aldehydes present.

The Seyewitz-Bardin method apparently cannot be used for the determination of acrolein, glycolic aldehyde, cyano-acetaldehyde, bromo-acetaldehyde, β -chloropropionaldehyde, amino- and imino-acetaldehydes. A long and fruitless search was made for a method whereby these aldehydes could be determined in the presence of their acetals. Finally it was found necessary to determine the extent of the reaction by determining the amount of water present in the equilibrium mixture. This was done by using cobaltous chloride in a colorimetric method. An accuracy better than 5% cannot be claimed for this method. Results obtained in this way agreed with the sulfite titration method when the latter could be used, as with acetaldehyde and heptaldehyde.

The pink crystals of cobaltous chloride were dehydrated by heating over a gas flame. A saturated solution of the dried salt was made in absolute alcohol, and three to five drops of this solution (depending on the amount of water present) was used as an indicator for each 5 cc. of solution. It was found that the color of the cobaltous chloride was a function not only of the amount of water but also of the amount of acetal present, but the color was not influenced by the free aldehyde, as with acetaldehyde, heptaldehyde and acrolein.

The amount of water at equilibrium was determined by comparing a 5cc. sample of the reaction mixture containing indicator with a set of standards which were prepared in the following way.

In a series of test-tubes previously cleaned and dried were put equimolecular amounts of water and of the acetal under investigation; the volume of each standard was made up to 5 cc. with absolute alcohol and the cobalt chloride indicator added. By comparing the color of the sample with that of the standards the amount of water in the equilibrium mixture could be determined. Since the amounts of acetal and water for each standard were small, separate solutions containing a known weight of acetal in absolute alcohol (Solution I) and a known weight of water in absolute alcohol (Solution II) were made up in volumetric flasks, and from these the necessary amounts of each were used and absolute alcohol then added to each tube to make the total contents equal to 5 cc.

To illustrate the use of this method an actual case will be given in detail.

In a reaction tube were placed

7.255 g.	Chloropropylal	0.0435 mole	7.36 cc.
0.785 g.	Water	.0436 mole	0.79 cc.
23.04 g.	Ethanol-catalyst (HCl)	.479 mole	<u>28.10 cc.</u>
			36.25 cc.

Several days later standards were prepared by using ordinary test-tubes, previously thoroughly cleaned and dried, and putting into them the indicated amounts of Solutions I and II. Solution I contained 10.014 g. of β -chloropropionaldehyde acetal and was made up to 25 cc. with absolute alcohol; Solution II contained 4.346 g. of water and was diluted with absolute alcohol to 50 cc.

No.	G., water	Cc., soln. II	G., acetal	Cc., sol. I	Cc., abs. alc.
1	0.0870	1.00	0.885	2.01	1.96
2	.0521	0.60	.488	1.20	3.20
3	.0261	.30	.242	0.64	4.06
4	.0191	.22	.177	.44	4.34
5	.0174	.20	.161	.40	4.40

A 5cc. sample was withdrawn from the reaction tube and to each of the standards and sample 3 drops of the cobalt chloride indicator was added. A color comparison of the sample with the standards showed it to be like 1. The next day a new set of standards in the vicinity of 1 was made but with less water variation, and in this way it was found that the acetal-equilibrium mixture corresponded to the standard containing 0.0912 g. of water per 5 cc. Thus the amount of unhydrolyzed acetal was found to be 84%.

Calculation of Equilibrium Constants and Affinity Values

The values for K_e listed in Table I are mean values and the manner in which they were obtained, especially where the equilibrium point was determined colorimetrically, is illustrated in the case of glycolic aldehyde. The extreme values of K_e for this aldehyde were found to be 0.0150 and 0.0272, giving for $-RT \ln K$ 2480 units and 2140 units, respectively, of which the average is 2310 units, corresponding to $K_e = 0.0202$; and $-RT \ln K$ becomes 2300 ± 180 units. K_e and $-RT \ln K$ were obtained in a similar manner for other aldehydes.

$$-RT \ln K = 1.9885 \times 298 \times 2.3026 \times \log_{10} k$$

Summary

The equilibrium constants for the reaction of ethanol with amino-acetaldehyde, bromo-acetaldehyde, cyano-acetaldehyde, imino-acetaldehyde, β -chloropropionaldehyde, glycolic aldehyde, acrolein and crotonic aldehyde, heptaldehyde, propionaldehyde, acetaldehyde, butyraldehyde and cinnamaldehyde have been given.

The values of $-RT \ln K$ have been calculated and used as the basis for a comparison of the relative affinity manifested by the various aldehydes in the acetal reaction.

It has been noted that the effect of a given substituent upon affinity in the acetal reaction is neither quantitatively nor qualitatively constant. The same substituent in some cases increases and in others decreases affinity.

Methods for synthesis of several acetals are given and some of their physical constants have been determined.

MADISON, WISCONSIN

THE OSMOMETRIC METHOD OF DETERMINING THE MOLECULAR WEIGHTS OF PROTEINS

BY GILBERT ADAIR¹

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In a recent paper Svedberg and Nichols² state that the osmotic pressure method of measuring the molecular weights of proteins is rendered quite uncertain by the Donnan equilibrium. Svedberg and Fåhræus³ stated that conflicting results, obtained by different investigators of the molecular weight of hemoglobin, were partly due to the difficulty of measuring osmotic pressures against semipermeable membranes and partly due to the Donnan effect.

An explanation of these difficulties has been suggested.⁴ The conflicting results referred to by Svedberg had been obtained with hemoglobin equilibrated with water of unknown hydrogen-ion concentration. New measurements⁴ showed that deviations from the isoelectric point led to abnormally high osmotic pressures on account of the excess of ions inside the membrane.

Unfortunately, Svedberg and Fåhræus did not refer to any of the papers on the osmotic pressure of hemoglobin published in 1924 and 1925, which showed that the membranes gave true equilibria,^{4,5,6} and the molecular weights corrected for the ion distribution effects were the same as the figure they obtained by the ultra-centrifugal method, namely, 62,000–71,000 for purified horse hemoglobin.

The osmometric data for the hemoglobins of various species have been given in the papers referred to as follows: hemoglobin of man, the horse and the sheep (solvent *N*/10 NaCl, etc.);⁴ hemoglobin of man and the ox (solvent salts of red corpuscle);⁶ hemoglobin of the horse and the sheep (solvent, distilled water).⁴ All the molecular weights agreed to within 10% of 66,800, which is four times the equivalent calculated from iron analyses.

The agreement of the results with different salt solutions affords a check on the accuracy of the membrane equilibrium corrections in the case of hemoglobin. The empirical correction formula⁵ which was pro-

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² Svedberg and Nichols, *THIS JOURNAL*, **48**, 3081 (1926).

³ Svedberg and Fåhræus, *ibid.*, **48**, 430 (1926).

⁴ Adair, *Proc. Roy. Soc. (London)*, **109A**, 292 (1925).

⁵ Adair, *Proc. Camb. Phil. Soc. (Biol.)*, **1**, 75 (1924).

⁶ Adair, *Proc. Roy. Soc. (London)*, **108A**, 627 (1925).

visionally suggested (because Donnan's assumptions concerning osmotic pressures apply only to ideal solutions) can be now withdrawn in favor of methods based on a new theoretical treatment of membrane equilibria.⁷

The corrections for hemoglobin were fairly accurate, but I had made no experiments on other proteins and the available data were difficult to interpret. Later work has shown that some of the provisional estimates⁵ require revision. The average mass of the protein particles in serum must be raised from 80,000 to about 100,000.

The data for egg albumin in concentrated ammonium sulfate solutions cannot yet be interpreted with confidence, but it is probable that 43,000 is nearer the truth than the earlier figure 66,000 which is now withdrawn.

Sørensen, on the basis of certain assumptions concerning the ionization of ammonium albuminate, formerly considered doubtful, deduced that the molecular weight of salt-free egg albumin would be about 34,000, an estimate recently confirmed by the centrifugal experiments of Svedberg and Nichols. Critics of the osmometric method might object that the influence of traces of alkali dissolved from the glass, and the hydrogen ions given off by the protein, might increase the osmotic pressure and the free energy of the protein and diminish the apparent molecular weight, but even in the case of acidic proteins like egg albumin, dissolved in distilled water, the hydrogen ions are unlikely to cause errors exceeding 20%, and it seems reasonable to claim that the agreement of the results obtained by different methods supports the view that the osmometer gives at least approximately correct results under suitable conditions.

Although the unequal distribution of ions is often advanced as a theoretical objection to the osmometric method, it is advantageous from the practical point of view because it facilitates the study of the activity coefficients of diffusible ions in the presence of proteins, an important point when the protein systems are studied as a whole.

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⁷ Adair, *Proc. Roy. Soc. (London)*, (in press).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DENVER]

THE SOLUBILITY OF NON-RADIATED CHOLESTEROL IN LIQUID AMMONIA

BY REUBEN G. GUSTAVSON AND JOHN B. GOODMAN

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Franklin and Kraus have pointed out the marked similarity of water and liquid ammonia as solvents, and determined the solubility in liquid ammonia—generally at atmospheric pressure (-33.35°)—of about two hundred inorganic and two hundred and fifty organic compounds.¹

This work was a continuation of the work of Gore.²

The work reported was largely qualitative. Franklin and Kraus report cholesterol as insoluble in liquid ammonia.³

Liquid ammonia has recently been used in this Laboratory to separate the female sex hormone from cholesterol.⁴

Advantage was taken of the insolubility of cholesterol in liquid ammonia by Koch, Cahan and Gustavson in the concentration of the antirachitic factor in irradiated cholesterol.⁵

The above work has made a quantitative study of the solubility of cholesterol in liquid ammonia highly desirable.

Method of Procedure

The cholesterol used was purified by several crystallizations from acetone and melted sharply at 147° . After preparation, the cholesterol was shielded from all light rays to preclude the possibility of radiating any considerable portion of it. The reaction tubes used in the experiments were of "T" shape, very similar to the type used by Franklin in his earlier experiments. Their use and manipulation can be best shown by the description of a typical determination.

A weighed amount of cholesterol was placed in a small filter paper. The whole was rolled up in the form of a small capsule and tied with cotton thread. Both thread and filter paper were previously extracted with liquid ammonia in a closed Soxhlet system. The capsule was placed in one leg of the reaction tube and covered with 3–5 cc. of anhydrous liquid ammonia. The tube was then sealed off. The study of the temperature effect on solubility was accomplished by immersing the "T" tube in a water thermostat accurately maintained at the required temperature. The tube was frequently shaken to facilitate the dispersion of the solute throughout the solvent. Tubes were allowed to remain in the thermostat for 3,

¹ Franklin and Kraus, *Amer. Chem. J.*, **20**, 820 (1898).

² Gore, *Proc. Roy. Soc. (London)*, **20**, 441 (1872).

³ Ref. 1, p. 834.

⁴ Frank and Gustavson, *J. Am. Med. Assoc.*, **84**, 1715 (1925).

⁵ Koch, Cahan and Gustavson, *J. Biol. Chem.*, **67**, No. 2, lii (1926).

4, 5, 6 and 7-day periods. No increase in the quantity of cholesterol dissolved was found after 72 hours, showing that equilibrium had been established. The temperature at -38° was maintained by immersing the tube in liquid ammonia contained in a Dewar flask open to the atmosphere (630 mm. barometric pressure). The cholesterol-saturated liquid ammonia was poured over into the other leg of the tube and the volume of the solution taken at 20° . The ammonia was then distilled back by carefully warming the solution and cooling the tube containing the capsule. Care had to be exercised at this point to avoid an error due to foaming. Since the quantity of cholesterol soluble in 3-5 cc. of liquid ammonia at low temperatures is small, the error introduced in weighing would be correspondingly larger.

The solubility at -38° was checked by the following method, which insured obtaining a saturated solution.

A "I" tube was prepared with a constriction in the side arm and a piece of cotton was placed in this constricted portion of the tube. A capsule containing cholesterol was placed in the other leg of the tube, covered with liquid ammonia and sealed off in the usual manner. The tube was placed in a water-bath at 45° and shaken frequently. On cooling to room temperature the liquid became turbid due to precipitation of the cholesterol. The tube was then placed in a Dewar flask containing liquid ammonia and allowed to stand for 24 hours.

The ammonia with some suspended cholesterol was filtered through the cotton into the other leg of the tube. The whole tube was immersed in liquid ammonia during this part of the operation. The ammonia was then distilled back in the usual manner. No weighable residue remained. The Liebermann-Burchardt test was negative.

The temperature range above 49° was not investigated because of the high pressures developed in the tubes at elevated temperatures.

The results in Fig. 1 are shown in milligrams of cholesterol per 100 cc. of liquid ammonia. The results in each case are the average of four determinations. The tabulation below gives the average weight of chole-

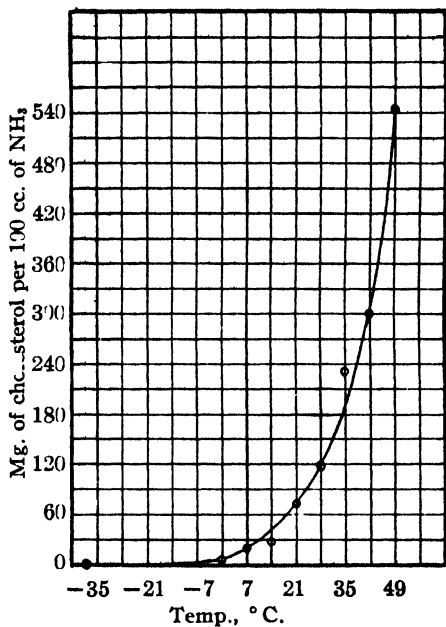


Fig. 1.

terol extracted, the average volume of liquid ammonia and the average solubility of the cholesterol in milligrams per 100 cc. of liquid ammonia.

TABLE I
THE SOLUBILITY OF NON-RADIATED CHOLESTEROL IN LIQUID AMMONIA

Temperature, °C.	Av. vol. of ammonia, Cc.	Av. wt., mg.	Av. solubility, mg. per 100 cc.
-38	4.00	0.00	0.00
0	4.05	0.25	6.16
7	4.13	0.83	20.2
14	4.05	1.10	27.2
21	3.30	2.40	72.6
28	3.20	3.75	117.2
35	3.70	8.60	232.2
42	3.25	9.80	301.2
49	3.95	21.55	545.0

The assistance of a grant from the National Research Council for the study of the isolation and purification of the female sex hormone is gratefully acknowledged.

Summary

1. The solubility of cholesterol in liquid ammonia at temperatures ranging from -38 to $+49^{\circ}$ has been determined.
2. The solubility at -38° is beyond the sensitiveness of the Liebermann-Burchardt test.
3. Liquid ammonia can be used to separate certain preparations from cholesterol.

DENVER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE REARRANGEMENT OF ACID AZIDES AND HYDROXAMIC ACIDS OF GEOMETRICAL ISOMERS

BY LAUDER W. JONES AND J. PHILIP MASON¹

RECEIVED MAY 4, 1927

PUBLISHED OCTOBER 5, 1927

In an article by Jones and Wallis² an account of the rearrangements of compounds with optically active radicals was presented. It was shown that *d*-benzylmethylacetazide, dissolved in benzene, rearranged at room temperatures ($10-35^{\circ}$) and that an optically active product, *d*-benzylmethyl methyl isocyanate, $(C_7H_7)(CH_3)CH.N=C=O$, and nitrogen (97%) were formed. These results suggested the experiments described in the following article.

¹ This paper is based upon a thesis submitted by J. Philip Mason to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

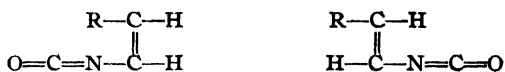
² Jones and Wallis, *THIS JOURNAL*, **48**, 169 (1926).

The problem may be stated as follows. If geometrical isomers in which the radicals of *cis* and *trans* configurations are directly attached to the group —CO.Nxy in such derivations as hydroxamic acids or acid azides undergo rearrangement, will the *cis* and *trans* configurations of their radicals be retained in the organic products of rearrangement?

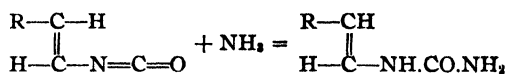
Two pairs of *cis-trans* isomers, namely, cinnamic acid and allocinnamic acid, and crotonic and isocrotonic acids, were chosen for investigation. It was found that the azides offered less experimental difficulty than the hydroxamic acids. The two space isomers are represented by the formulas



If these pairs of isomers, in which R stands for C_6H_5 or CH_3 , rearrange and the configurations of the styryl and *iso*-allyl radicals persist, then two different isocyanates should result in each case



Furthermore, addition of ammonia to these isocyanates should yield *two pairs of space isomeric monosubstituted ureas*, for example,



But if the styryl and *iso*-allyl radicals change and the "labile" configuration gives place to the "stable" configuration, only one isocyanate would result in each case and consequently *only one urea* would be formed from each pair of isomeric azides.

Results of the Study of Azides

The azides of the four different acids were prepared by the action of powdered sodium azide upon the acid chlorides dissolved in absolute ether or in benzene. The azide of cinnamic acid has been described by Forster.³ It is a solid which melts at 86° , accompanied by decomposition. A solution of this azide in benzene did not evolve nitrogen until a temperature between 75 and 80° was reached. In contrast to this behavior, the azide of allocinnamic acid, during its preparation by the action of sodium azide upon the acid chloride dissolved in ether, lost nitrogen at room temperature continuously; about 100 cc. of nitrogen was collected during the course of the reaction (six–seven hours). The azide of cinnamic acid may be crystallized from boiling ether without suffering any decomposition. No attempt was made to isolate the azide of allocinnamic acid, because every precaution was being taken to prevent a change to the more stable cinnamic form, and at the temperature necessary to cause

³ Forster, *J. Chem. Soc.*, 95, 437 (1909).

sodium azide and the acid chloride to react decomposition was unavoidable and a mixture of azide and isocyanate was always obtained.

The behavior of ether solutions of the azides described above seems to justify the conclusion that the azide of allocinnamic acid existed in solution and decomposed to give nitrogen and an isocyanate at a temperature appreciably lower than that required to affect the azide of cinnamic acid.

The azides obtained from crotonic and isocrotonic acids did not show so pronounced a difference in reactivity.

The conversion of the isocyanates into monosubstituted ureas, a reaction carried out by passing the calculated amount of ammonia gas into cold ether solutions of the isocyanates, seemed to offer the best chemical method of determining whether or not the radicals in the isocyanates had retained their original configurations. When these experiments were performed, only *one monostyryl urea*, $C_6H_5CH=CH-NH-CO-NH_2$ (m. p. 142–143°), was obtained and, similarly, from crotonic and isocrotonic azides only *one mono-iso-allyl urea*, $CH_3-CH=CH-NH-CO.NH_2$ (m. p., 122°), resulted.

These observations lead to the conclusion that during rearrangement the labile radicals assume the more stable configurations; for it is not likely that the action of ammonia at 0° upon the isocyanates would cause the radicals to change their configurations from *cis* to *trans*.

Results of the Study of Hydroxamic Acids

Mention has been made of complications encountered in experiments with hydroxamic acids. Cinnamhydroxamic acid has been studied by several investigators.⁴ The potassium salt of the benzoyl ester of this hydroxamic acid, $C_6H_5CH=CH-CO.NKO.CO.C_6H_5$, was prepared and a solution of it in water was heated to cause rearrangement. In reactions of this kind, the isocyanates first produced are usually hydrolyzed and *sym.*-disubstituted ureas are obtained as the chief product of the reaction. It was hoped that these ureas might be employed to answer the question concerning the behavior of the radicals discussed above.

When the experiment was performed, no *sym.*-distyryl urea, $(C_6H_5CH=CH-NH)_2CO$, could be isolated. However, when the azide of cinnamic acid was heated with water, it behaved normally; the chief product of the reaction was *sym.*-distyryl urea.

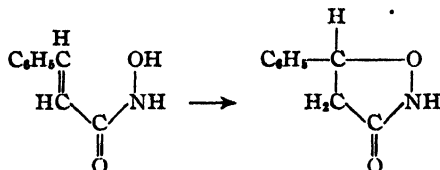
Thiele and Pickard⁵ stated that the potassium salt of this benzoyl ester of cinnamhydroxamic acid heated with water gave "no definable transformation product." We have isolated a perfectly definite compound, a colorless solid which melted at 152°. It was not the disubstituted urea. The nitrogen content was almost exactly that required for cinnamhydrox-

⁴ Rostolski, *Ann.*, **178**, 214 (1875). Thiele and Pickard, *Ann.*, **309**, 189 (1899). Velardi, *Gazz. chim. ital.* [2] **34**, 66 (1904).

⁵ Thiele and Pickard, *Ann.*, **309**, 189 (1899).

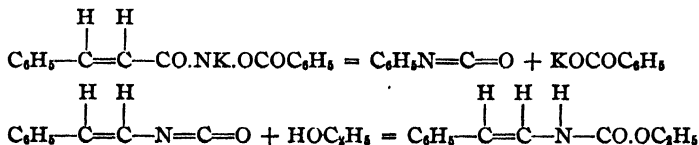
amic acid, but the properties of the two compounds were totally different. At first it was thought that it might be γ -phenyl- α -isoxazolone, which melts at 152°.

The percentage of nitrogen in the compound was found to be almost exactly that required by this isoxazolone. But it is difficult to see how this particular isoxazolone could be formed in the reaction. It is evident that by intramolecular addition cinnamhydroxamic acid might yield α -phenyl- γ -dihydro-isoxazolone; but the isoxazolones possess very pro-



nounced acid properties and are readily soluble in solutions of the alkalis in the cold, whereas our compound was not soluble even in boiling alkalis. We hope to be able to identify the substance later.

In this connection, it is interesting to note that the potassium salt of the benzoyl ester of cinnamhydroxamic acid dissolved in boiling absolute alcohol shows a normal behavior; styryl urethan is formed by addition of alcohol to the isocyanate. This observation was also made by Thiele and Pickard.



Experimental Part

I. Rearrangement of the Azide of Cinnamic Acid

Preparation of the Azide.—The method employed was similar to the one used by Forster.⁶

Sodium azide (Kahlbaum) was purified by dissolving it in the minimum amount of water and reprecipitating it by the addition of acetone. Then, 20 g. of dry, finely-powdered azide (60% excess) was suspended in 120 cc. of absolute ether and 20 g. of cinnamyl chloride was added. This mixture was stirred for eight or ten hours at room temperature. The solid material was collected on a filter and washed with water to remove sodium chloride and sodium azide, and the azide was purified by crystallization from ligroin (b. p. 60–80°). Evaporation of the ether filtrate to one-half its original volume gave additional crystals of the azide. In all about 2.5 g. of pure azide (m. p. 86°) was obtained.

Preparation of Styryl Isocyanate: $\text{C}_6\text{H}_5\text{CH=CH-N=C=O}$.—A solution of 5 g. of cinnamic acid azide in 25 cc. of benzene dried over sodium was placed in a flask connected with a reflux condenser protected at the top by a calcium chloride tube. The

⁶ Forster, *J. Chem. Soc.*, 95, 437 (1909).

solution was heated to a temperature just below the boiling point until no more nitrogen was evolved. After removing the benzene, the isocyanate was distilled under diminished pressure (12 mm.). It boiled at 107°. About 3 g. of pure isocyanate was obtained.

sym.-Distyryl Urea: $(C_6H_5CH=CH-NH)_2C=O$. *Action of Water upon the Isocyanate.*—Several grams of styryl isocyanate was suspended in water heated to 50°. The isocyanate was decomposed slowly. A white solid was formed which, after crystallization several times from dil. alcohol, melted at 214°. It was soluble in alcohol and in ethyl acetate and insoluble in ether and ligroin.

Anal. Subs., 0.3723 g.: N, 35.5 cc. (29°, 758 mm.). 50% KOH used. Calcd.: N, 10.6. Found: 10.7.

Rearrangement of Cinnamic Acid Azide in the Presence of Water.—A suspension of 3 g. of the azide in 75 cc. of water was heated nearly to boiling for half an hour. A yellow solid was formed and the solution became turbid. The solid weighed 2.2 g. Treatment of it with ether removed the yellow color and recrystallization from dil. alcohol gave *sym.*-distyryl urea; m. p., 214°.

The turbid solution filtered from the solid was extracted with ether and the ether evaporated. This gave a yellow, gummy product which possessed the peculiar aldehyde odor noticed in the rearrangement of the benzoyl ester of cinnamhydroxamic acid described in the latter part of this article. The yellow material finally became solid. It was treated with a small amount of benzene to remove the yellow color and recrystallized from dil. alcohol. This gave distyryl urea; m. p., 213°.

The rearrangement of the azide in water was also carried out in an atmosphere of carbon dioxide in order to measure the nitrogen evolved. Bubbles of nitrogen were not observed until the temperature of the water reached 75 to 80°. Thus, 0.3135 g. of the azide gave 42.8 cc. of nitrogen at 22° and 743 mm. over 50% potassium hydroxide. This corresponds to 94.8% of the nitrogen required for complete decomposition according to the equation.

Monostyryl Urea: $C_6H_5CH=CH-NH-CO-NH_2$.—A solution of 1.6 g. of the azide of cinnamic acid in 10 cc. of dry benzene was heated to bring about the rearrangement of the azide. The benzene was removed and the isocyanate dissolved in 10–15 cc. of dry ether. The flask containing the solution was cooled by ice water, and dry ammonia gas passed into the ether. A pale yellow precipitate formed; wt., 1.1 g.; m. p., 140–143°. Recrystallization of it from dil. alcohol gave a colorless solid which melted at 143°. It was soluble in acetone, in alcohol and in ethyl acetate, and insoluble in water and in ether.

Anal. Subs., 0.2815: N, 41.5 cc. (21°, 757.5 mm.). 50% KOH used. Calcd.: N, 17.3. Found: 16.9.

II. Rearrangement of the Azide of Allocinnamic Acid

Preparation of Allocinnamic Acid.—Allocinnamic acid was prepared according to the method of Liebermann and Scholz⁷ and of Michael⁸ by the reduction of α -bromo-allocinnamic acid. The starting material in the preparation was cinnamic acid. The yield of allocinnamic acid (m. p. 67°) was small; not more than 7 g. of pure substance was obtained from 100 g. of cinnamic acid in any of our experiments.

Preparation of Allocinnamic Acid Azide.—The chloride of allocinnamic acid was made by treating the acid (3.3 g.) dissolved in a small amount of ether with an excess of thionyl chloride at 0°. The mixture stood for half an hour in an ice-bath. Ether and excess of thionyl chloride were removed by evaporation in a vacuum desiccator.

⁷ Liebermann and Scholz, *Ber.*, 25, 950 (1892).

⁸ Michael, *Ber.*, 34, 3648 (1901).

The acid chloride could not be distilled without being converted into the more stable chloride of cinnamic acid, so it was used directly. Finely powdered sodium azide (5 g.) was suspended in absolute ether contained in a 3-necked flask, which was connected with a carbon dioxide generator and also with an azotometer charged with a 50% solution of potassium hydroxide. After the system was thoroughly filled with carbon dioxide, an ether solution of the acid chloride (3.5 g.) was introduced through a dropping funnel.

This mixture was stirred for six or seven hours. During this time about 100 cc. of nitrogen gas collected in the azotometer. This implied that the azide of allocinnamic acid had formed and suffered decomposition and rearrangement at room temperature; the azide of cinnamic acid did not yield nitrogen under these conditions.

The Monostyryl Urea.—The ether solution which contained the isocyanate was filtered from the solids. It was cooled and treated with ammonia gas. A white precipitate weighing about 0.3 g. was collected and washed with water to remove any ammonium chloride. After crystallization from dil. alcohol it melted at 142°.

It is probable that the decomposition of the azide was not complete. The evolution of nitrogen took place slowly at room temperature. It did not seem desirable to hasten decomposition by increasing the temperature since this might cause a conversion of the allocinnamic form.

These results show that the same monosubstituted urea was obtained in the two experiments. It seems probable, therefore, that the isocyanates were identical.

III. Rearrangement of the Azide of Crotonic Acid

Preparation of the Azide: $\text{CH}_3\text{CH}=\text{CH}-\text{CO}-\text{N}_3$.—Crotonyl chloride was made by the action of thionyl chloride upon an excess of crotonic acid, first at room temperature and finally at 50–60°. It was separated by fractional distillation (b. p., 124°).

An ether solution of 21 g. of crotonyl chloride in which 23 g. of sodium azide was suspended was stirred mechanically for two days. An azotometer was connected with the flask containing the mixture. No nitrogen was evolved during the reaction. The ether solution was filtered and evaporated in a current of dry air. This gave 14 g. of the azide. It was a clear liquid possessing a sharp odor.

A sample of it was placed in a melting-point tube and, after inserting a glass thread, was heated slowly. At 30–40° an occasional bubble of gas was given off; at 75–85°, the evolution of nitrogen became very rapid.

To test the purity of the liquid, a weighed sample dissolved in benzene was decomposed in an apparatus from which air had been displaced by carbon dioxide, and the nitrogen was collected in an azotometer over a solution of potassium hydroxide. A correction was made for the vapor pressure of benzene.

Anal. Subs., 0.2470: N, 44.3 cc. (18°, 745 mm.). Vapor pressure of benzene at 18°, 68.9 mm. Calcd.: N, 49.8 cc. Found: 37 cc.; 74.2% azide in liquid.

Mono-*iso*-allyl Urea, $\text{CH}_3-\text{CH}=\text{CH}-\text{NH}-\text{CO}-\text{NH}_2$.—Seven g. of the impure liquid azide was placed in a clean, dry flask, attached to a reflux condenser, and heated on a water-bath until no more nitrogen was evolved. The liquid, chiefly *iso*-allyl isocyanate, possessed a very acrid and suffocating odor. Absolute ether was added to the residue and a current of dry ammonia gas was then passed through the solution as long as a precipitate was obtained. The white precipitate, collected on a filter and dried, weighed 2 g. Recrystallized from a mixture of hot ethyl acetate and chloroform by the addition of ligroin, it formed pure white crystals which melted at 122°.

It is very soluble in alcohol and in acetone, quite soluble in ethyl acetate, in chloroform and in warm water, from which it does not separate in good crystalline form. It is insoluble in ligroin, in benzene and in ether.

Anal. Subs., 0.1211: N, 30.4 cc. (32.5°, 757.3 mm.). 50% KOH used. Calcd.: N, 28. Found: 27.8.

IV. Rearrangement of the Azide of Isocrotonic Acid

Isocrotonic acid (Kahlbaum) purified according to the method suggested by Wislicenus⁹ was converted into isocrotonyl chloride by the action of a little less than the calculated amount of thionyl chloride upon an ether solution of the acid. Isocrotonyl chloride cannot be distilled at atmospheric pressure without isomerization to give the more stable crotonyl chloride. To avoid any change of this kind the ether was removed carefully and the acid chloride obtained from 10 g. of isocrotonic acid used directly.

Preparation of the Azide of Isocrotonic Acid.—An ether solution of this chloride treated with 14 g. of sodium azide was stirred for two days. During the first 12 hours the mixture was kept at a temperature between 15 and 20°. No nitrogen was formed so the temperature was increased to 25–28°. This caused a slow evolution of nitrogen.

Mono-*iso*-allyl Urea.—After two days the ether solution was filtered, cooled and treated with dry ammonia gas. This gave a small amount of colorless solid which was recrystallized from a mixture of ethyl acetate and chloroform by the addition of ligroin. It melted at 122° and was identical with the urea obtained from the azide of crotonic acid as described above.

V. Rearrangement of Cinnamhydroxamic Acid

Preparation of Cinnamhydroxamic Acid.—Although this compound has been prepared by several investigators,⁴ we found it more satisfactory to prepare it by the method used by Jones and Hurd in other preparations.¹⁰

The acid chloride of cinnamic acid was prepared by warming the acid with a 10% excess of thionyl chloride at 50°. When the reaction was complete, the liquid, still warm, was transferred to a distilling flask, the excess of thionyl chloride drawn off by means of a water pump, and the acid chloride distilled; b. p., 101° (2 mm.).

Free hydroxylamine was prepared by the method of Lecher and Hofmann¹¹ with the apparatus similar to that used by Hurd and Brownstein.¹²

A solution of 24 g. of cinnamic acid chloride in 60 cc. of dry benzene was added slowly to a suspension of 12 g. of free hydroxylamine in 100 cc. of dry benzene, while the flask was shaken and cooled in ice water. The reaction took place immediately; a white, viscous substance was formed. After all of the chloride was added the mixture was shaken for a few minutes and then filtered. The precipitate was washed twice by suspending it in water. It was collected and dried in a vacuum desiccator; wt., 24 g. The acid was recrystallized from hot ethyl acetate by the addition of ligroin. The first crystallization usually yielded an oil which solidified readily as it became cool. The melting point was finally raised to 119.5°. Thiele and Pickard gave 111° as the melting point.

Anal. Subs., 0.4749: N, 37.6 cc. (22.5°, 754 mm.). 50% KOH used. Calcd.: N, 8.95. Found: 9.03.

As a further check upon the constitution of the compound, a sample was hydrolyzed by heating it with 6 *M* hydrochloric acid. The ratio of cinnamic acid to hydroxylammonium chloride formed was found to be 1:1.

An attempt to prepare the hydroxamic acid by adding a few drops of water to an ether solution of the acid chloride in which equivalent quantities of sodium carbonate

⁹ Wislicenus, *Vierteljahrsschr. Naturforsch. Ges. Zürich*, **41**, 270–293 (1897).

¹⁰ Jones and Hurd, *THIS JOURNAL*, **43**, 2439 (1921).

¹¹ Lecher and Hofmann, *Ber.*, **55B**, 912 (1922).

¹² Hurd and Brownstein, *THIS JOURNAL*, **47**, 68 (1925).

and hydroxylammonium chloride were suspended resulted in the formation of a mixture of the mono- and dicinnamhydroxamic acids.

Preparation of the Benzoyl Ester of Cinnamhydroxamic Acid.—The best method for the benzoylation of the hydroxamic acid was found to be that of Heidelberger and Jacobs.

A solution of 6.55 g. of cinnamhydroxamic acid in a mixture of 30 cc. of glacial acetic acid and 30 cc. of a saturated solution of sodium acetate was shaken with 6 cc. of benzoyl chloride added in small portions, while the flask was immersed in ice water. After a short time the benzoyl ester separated as a white solid. One crystallization of it from hot ethyl acetate with addition of ligroin gave 8.5 g. of benzoyl ester, which melted at 150–152°. Further recrystallization from hot ethyl acetate and ligroin, or from hot dil. alcohol, yielded pure white crystals which melted sharply at 156.5°. Thiele and Pickard gave 144° as the melting point.

Preparation of the Potassium Salt of the Benzoyl Ester of Cinnamhydroxamic Acid.—The benzoyl ester was only slightly soluble in cold alcohol and less soluble in ether. On this account, the ordinary method of preparing a potassium salt of this class was not satisfactory. Acetone was found to be the most suitable solvent. In a typical experiment, 7.95 g. of benzoyl ester was dissolved in 130 cc. of warm, dry acetone, and a cold solution made by dissolving 1.02 g. of potassium in 30 cc. of absolute methanol was added. The potassium salt formed immediately as a white precipitate. The mixture was cooled rapidly by shaking the flask in ice water. Addition of about 100 cc. of dry ether increased the yield; weight of dry salt, 8.2 g. The sodium salt was prepared by the same method.

Anal. Subs., 0.0561: Na_2SO_4 , 0.0140. Calcd. for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{NNa}$: Na, 7.96. Found: 8.08.

Rearrangement of the Potassium Salt in Water.—The potassium salt was only slightly soluble in water at room temperature, 2.5 g. dissolving in about 150 cc. of water. When this solution was heated, it became turbid at 40–45°. The precipitate could not be coagulated completely by any of the usual methods. By filtration, only a very small amount of a white precipitate was obtained. When it was crystallized from hot ethyl acetate or hot benzene, it melted at 152°. The same product was obtained when dicinnamhydroxamic acid was treated with an equivalent amount of sodium carbonate dissolved in water. During the rearrangement, a peculiar odor resembling that of benzaldehyde was noticed, but no aldehyde was ever detected when the solution was tested.

Anal. Subs., 0.0368: N, 2.7 cc. (21°, 760 mm.). 50% KOH used. Found: N, 8.5.

Summary

The azides of two pairs of *cis-trans* isomers, namely, cinnamic acid and allocinnamic acid, crotonic and isocrotonic acids have been prepared and caused to undergo rearrangement. The isocyanates formed by rearrangement were converted into monosubstituted ureas by addition of ammonia. Only one monostyryl urea and one *iso*-allyl urea could be obtained. This seems to indicate that during rearrangement the configurations of the styryl and *iso*-allyl radicals are changed and only the stable *trans* configuration appears in the ureas and undoubtedly, also, in the first product of rearrangement, the isocyanates.

The rearrangement of the potassium salt of the benzoyl ester of cinnamhydroxamic acid was studied. A definite product (m. p., 152°) was

obtained. It was not the *sym.*-disubstituted urea expected. It has not been identified.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.]

THE USE OF NITROGEN TETROXIDE IN PLACE OF NITRIC ACID IN ORGANIC NITRATIONS¹

BY L. A. PINCK

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It has been previously observed that when nitrogen tetroxide is allowed to react with organic substances, oxidation, nitration or diazotization may take place. In general, the experience of previous workers has been that both oxidation and nitration take place when a solution of nitrogen tetroxide in an organic substance is allowed to stand either in the dark or in sunlight for several weeks to several months. With nitro arylamines,² nitrogen tetroxide acts as a diazotizing reagent. It has also been found that solutions of nitrogen tetroxide in toluene and benzene form explosive mixtures.³

The reactions of oxides of nitrogen with organic substances described in the literature, as well as some preliminary experiments conducted in the course of this investigation, indicate that the direct nitration of organic substances with oxides of nitrogen is neither safe nor economically feasible, the chief objections being: (1) slowness of nitration at moderate temperature, (2) oxidation and (3) possible explosions at higher temperatures.

The present paper describes a study of the conditions governing the nitration of a number of aromatic compounds with nitrogen tetroxide in the presence of sulfuric acid.

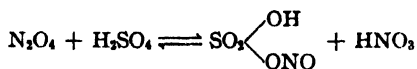
Theoretical

The fact that nitric acid oxidizes and only partially nitrates an organic substance, whereas a mixture of nitric and sulfuric acids yields a complete nitration, led to the belief that oxidation and explosion hazard might be avoided by using sulfuric acid in conjunction with the oxides of nitrogen. Sulfuric acid mixed with nitrogen tetroxide serves a purpose quite distinct from its use in the mixed acid nitration, for not only does it function as a dehydrating reagent, but it has the additional function of forming nitric acid *in situ* as shown in the following equation

¹ Presented before the Division of Organic Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Virginia, April 11-16, 1927.

² Houston and Johnson, *THIS JOURNAL*, 47, 8011 (1925).

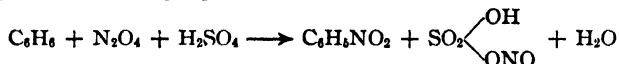
³ Raschig, *Z. angew. Chem.*, 35, 117 (1922).



This equilibrium can be shifted practically completely to the right, for, according to the law of mass action $\frac{(\text{N}_2\text{O}_4)(\text{H}_2\text{SO}_4)}{(\text{HSO}_3\text{N})(\text{HNO}_3)} = K$, there are two factors involved in reducing the concentration of nitrogen tetroxide to a minimum, namely, the use of an excess of sulfuric acid and the constant removal of the nitric acid owing to its interaction with the organic substance, yielding a nitro compound.

The nitrosylsulfuric acid formed in the reaction and any unreacted sulfuric acid present in the mixture act as dehydrating reagents, thus facilitating the nitration of the organic substance.

In such a system, about 50% of the oxide of nitrogen is utilized in the nitration of the organic substance, and approximately 50% is combined with the sulfuric acid in the form of nitrosylsulfuric acid. The complete reaction for a single-step nitration for benzene, for example, can be represented by the following equation



The subsequent reaction of nitrosylsulfuric acid and water which one would expect is negligible, owing to the formation of a very stable solution of nitrosylsulfuric acid in concentrated sulfuric acid which stands dilution with water to some extent with the establishment of corresponding equilibria.

Nitration of Benzene

Work, therefore, was undertaken to determine the practicability of this method as applied to the nitration of benzene. The apparatus used in these experiments consisted of a wide mouthed bottle with a ground-glass joint bearing a mercury seal for a stirrer. Just below the neck of the bottle were sealed to it a dropping funnel and a capillary tube with a stopcock. In general, the method of procedure was as follows. To a solution in the bottle consisting of 1.05 moles of nitrogen tetroxide in 1.25 to 1.75 moles of sulfuric acid, having a concentration ranging between 85 and 95%, a mole of benzene was slowly added from the dropping funnel. During the addition the temperature of the reaction mixture was maintained at 5 to 15°, and subsequent to the mixing of the reactants the temperature was raised to 40–60°, the working temperature range being essentially that recommended in the ordinary nitration of benzene. The reaction mixture was agitated during the addition and afterwards until the reaction was complete, the total time for each run being five hours. The stopcock on the capillary tube was turned whenever there was an appreciable difference between the internal and external levels of the mercury in the seal of the stirrer.

The yields found were somewhat lower than the true yields, owing to the small losses in the various steps in the process. The quantity of material used in each of these experiments was relatively small (25 cc. of benzene), hence the sum total of the various losses was a fair percentage of the total, and it was believed that a few of the actual yields were similar to those obtained in commercial practice.

The data of the more significant experiments are recorded in the following table.

TABLE I
NITRATION OF BENZENE
Molecular ratio of N_2O_4 to C_6H_6 = 1.05

Expt. No.	Moles H_2SO_4^a	Concn. of H_2SO_4	Temp., °C.	Yield of nitrobenzene (steam distilled), %
1	1.25	95	40-50	81.3
2	1.50	95	50-60	89.5
3	1.75	95	55-60	94.4
4	1.25	85	40	70.2
5	1.50	85	40-50	80.7
6	1.50	90	40-50	86.3

^a Per mole of benzene.

An examination of the table shows that there are the following possible variables, namely, (1) ratio of nitrogen tetroxide to benzene, (2) ratio of sulfuric acid to benzene, (3) concentration of the sulfuric acid and (4) temperature.

With regard to the ratio of nitrogen tetroxide to benzene, it has been previously stated that theoretically they should be molecular. However, in practice a slight excess of the oxide of nitrogen is preferable, for the purpose of hastening the final stage of the nitration as well as taking care of any volatilization of the nitrogen tetroxide. Hence, a molecular ratio of 1.05 nitrogen tetroxide was selected and was found to be very satisfactory.

As shown by the experimental data, it is more desirable to use a large excess of sulfuric acid. By using a higher molecular ratio of sulfuric acid, for example, 1.75, the nitration can be carried out at higher temperatures (55-60°) without any appreciable loss of the oxide of nitrogen, and consequently the reaction is completed in a shorter period of time.

The concentration of the sulfuric acid is a very important factor which is dependent upon the nature of the substance to be nitrated and upon the quantity of sulfuric acid used. It is well known that in the nitration of substances which are readily nitrated lower acid concentrations are more desirable than "concentrated" or fuming sulfuric acid. By maintaining the molecular ratio of sulfuric acid to benzene constant, a variation in the concentration of the sulfuric acid from 85 to 95% effects a 9-11% increase in yield of nitrobenzene. However, the higher yields can be obtained by using greater quantities of sulfuric acid of the lower concentration.

The temperature is determined by the quantity and concentration of the sulfuric acid.

Nitration of Mononitrobenzene

When 2 moles of nitrogen tetroxide and from 2.5 to 3 moles of concentrated and fuming sulfuric acid per mole of benzene were used, several unsuccessful attempts to effect a two-step nitration were made.

However, a 93.4% yield of dinitrobenzene was obtained by slowly adding a mole of nitrobenzene to a solution of 1.05 moles of nitrogen tetroxide in 2.8 moles of fuming sulfuric acid (containing 4.28 parts of free SO_3).

The effect owing to the variation of the molecular ratio and concentration of the sulfuric acid is shown in the following table.

TABLE II
NITRATION OF NITROBENZENE

Expt. No.	Moles of N_2O_4	Moles of H_2SO_4^*	Concn. of H_2SO_4	Time (hrs.)	Temp., °C.	Yield of di-nitrobenzene
1	1.1	2.8	104.3	1½	60-75	93.4%
2	1.05	2.0	104.3	1½	60-75	86.4
3	1.05	1.75	104.3	3	60-75	69.6
4	1.05	1.5	104.3	2½	60-70	49.3
5	1.1	2.7	95	2½	60-70	84.3
6	1.05	2.5	95	2½	55-70	55.0
7	1.05	2.0	95	2½	60-75	40.7
8	1.05	1.5	95	3	55-70	17.5

* Per mole of nitrobenzene.

Nitration of Toluene

Nitrotoluene was synthesized by adding a mole of toluene to a solution of 1.05 moles of nitrogen tetroxide in 1.6 moles of 95% sulfuric acid. The reaction mixture was agitated for three and one-half hours at a temperature of 50-55°, and at the end of the reaction the excess toluene was removed by vacuum distillation. The yield of nitrotoluene was 87.5% of the theoretical.

Nitration of Naphthalene

α -Nitronaphthalene was obtained by the reaction of 1.0 moles of naphthalene with a solution of 1.1 moles of nitrogen tetroxide and 1.5 moles of 95% sulfuric acid. The experimental procedure was similar to that used in the nitration of naphthalene with mixed acid. The yield of purified α -nitronaphthalene, recrystallized from alcohol, was 88.4% of the theoretical.

Summary

1. A method for the nitration of organic substances with nitrogen tetroxide in the presence of sulfuric acid is described, benzene, nitrobenzene, toluene and naphthalene being used as examples.

2. The method involves an intermediate reaction of the nitrogen tetroxide with the sulfuric acid whereby nitrating and dehydrating reagents are simultaneously formed.

3. The yields of the nitro compounds range from 87% to upwards of 90% of the theoretical.

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DECOMPOSITION OF FREE AND COMBINED CYSTINE WITH SPECIAL REFERENCE TO CERTAIN EFFECTS PRODUCED BY HEATING FISH FLESH

By L. H. ALMY

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Other investigators have studied the effect of acid and alkali hydrolysis of proteins upon the combined cystine, as shown in a review of the subject by Hoffman and Gortner.¹ The experimental evidence on the extent of the breaking down of cystine during acid hydrolysis is somewhat divided, but the destructive effect of alkali hydrolysis is generally accepted. The variability of the results obtained by different investigators is due to the lack of uniformity in experimental conditions. The method employed in the study here reported differs decidedly from those generally used. The results, therefore, may not be compared strictly with those of others. Briefly, the procedure consists in heating flesh in a sealed tube with the addition of little or no water or aqueous solutions. This method of heating was decided upon since it was desired to use a procedure which would imitate to a degree the conditions existing in a can of food material during the sterilization process. The purpose of the study was to gain sufficient information on the changes which take place during the heating of proteinaceous food products to afford a basis for the interpretation of the hydrogen sulfide content of the canned product.

Experimental Procedure

The flesh from fresh marine fish of various species was ground thrice to make a homogeneous sample. Twenty grams of the flesh, with or without the addition of other substances, was placed compactly in a 20 × 150 mm. test-tube of soft glass. The tube was sealed in the blast lamp and heated in a constant-temperature bath for 45 minutes. It was then opened and the heated product examined. Because of the nature of the tests, but one determination could be made on the contents of each tube.

For the determination of hydrogen sulfide, the tube was inverted in a beaker containing about 25 cc. of 0.6% zinc acetate solution and the tip of the tube was broken off beneath the surface of the liquid. The beaker, with the tube, was placed in a vacuum desiccator, the evacuation of which drew the gas in the tube through the zinc acetate solution, thus trapping any hydrogen sulfide contained in the air space above the flesh and rendering possible the quantitative determination of the hydrogen sulfide remaining after the heating. The tube was then carefully broken in the center. The contents were ground thoroughly in a mortar and finally washed into a cylinder for the determination of hydrogen sulfide by the methylene blue method.² This method estimates both the gas which is combined as sulfide and that which exists free in the flesh. The term "hydrogen sulfide" as used throughout this paper includes both forms.

For the estimation of cystine, the tube was opened, the flesh ground in a mortar

¹ Hoffman and Gortner, *THIS JOURNAL*, **44**, 341-360 (1922).

² Almy, *ibid.*, **47**, 1381-1390 (1925).

with about 50 cc. of water, the protein precipitated by the tungstic acid method of Folin and Wu,³ and the mixture diluted to 100 cc. with distilled water. The protein-free filtrate therefrom was then analyzed for cystine by Sullivan's method.⁴

Hydrogen-ion determinations were made either electrometrically⁵ by means of the hydrogen electrode, or colorimetrically, and sometimes by both methods, on the filtrate from 25% aqueous suspensions of the finely divided material.

For certain of the tests cystine dissolved in *N* hydrochloric acid solution was added to the flesh before the heating. The cystine solution was varied in concentration, but was always used in the proportion of 2 cc. to 50 grams of flesh. Two cc. of *N* sodium hydroxide solution was then added to neutralize the hydrochloric acid. Cysteine was likewise added in *N* hydrochloric acid solution, the hydrochloric acid of the cysteine hydrochloride having first been neutralized with dilute sodium hydroxide solution. Control samples were similarly treated with equivalent quantities of *N* hydrochloric acid and *N* sodium hydroxide solution.

Experimental Results

Effect of Heating on the *P_H* of the Product.—As variations in the H-ion concentration may cause differences in the results, it was necessary to determine the extent of the change in reaction produced by the heating in soft glass. It was found that the *P_H* of the material before and after heating seldom differed by more than 0.2 of a Sørensen unit. This observation is in general harmony with that of Esty and Cathcart,⁶ who found that soft glass tubes affected the H-ion concentration of vegetable juices heated therein less than the hard glass tubes.

Effect of Heat on Fresh and Stale Flesh

The flesh of strictly fresh fish seldom contains hydrogen sulfide. Of twelve species examined by the methylene blue method, only one gave a measurable quantity of the gas. As the flesh becomes stale, it may or may not give a positive test. The amount of hydrogen sulfide obtained on heating the flesh in a sealed tube, however, increased with the length of time the product was held prior to the heating (Table I). Although the *P_H* shifts from the acid toward the alkaline side, it does not seem to be a requisite that the flesh be neutral or alkaline to yield a considerable quan-

TABLE I

HYDROGEN SULFIDE LIBERATED FROM FRESH AND STALE FLESH ON HEATING FOR 45 MINUTES AT 120 °C.

Fish	Fresh		24 hours		After holding at room temperature		48 hours		72 hours	
	H ₂ S,	<i>P_H</i>	H ₂ S,	<i>P_H</i>	H ₂ S,	<i>P_H</i>	H ₂ S,	<i>P_H</i>	H ₂ S,	<i>P_H</i>
	mmg. per		mmg. per		mmg. per		mmg. per		mmg. per	
	100 g.		100 g.		100 g.		100 g.		100 g.	
Weakfish, <i>Cynoscion regalis</i>	33	6.5	3296	7.0	3859	7.1	..	7.3		
Rockfish, <i>Roccus lineatus</i>	34	6.0	59	6.3	1809	6.5	2922	6.6		

³ Folin and Wu, *J. Biol. Chem.*, **38**, 81 (1919).

⁴ Sullivan, *Public Health Reports*, **41**, 1030-1056 (1926).

⁵ Thanks are due to Mr. H. C. Waterman of the Food Control Laboratory of the Bureau of Chemistry for the H-ion measurements made in connection with this study.

⁶ Esty and Cathcart, *J. Infectious Diseases*, **29**, 29-39 (1921).

tity of the gas. None of these samples of flesh before heating gave a test for hydrogen sulfide except the rockfish sample at the 72-hour period, the amount being only 13.4 mmg. (micromilligrams) per 100 g.

Effect of Added Cystine and Cysteine on Hydrogen Sulfide Produced by Heating Flesh

In an effort to determine what part cystine or cysteine plays in the production of hydrogen sulfide on heating the flesh, the following experiment was made.

Twelve 40 g. portions of rockfish flesh were thoroughly mixed with varying quantities of *N* hydrochloric acid and *N* sodium hydroxide solution to give samples having Sørensen values ranging from *P_H* 5.0 to *P_H* 8.4. There were thus obtained four groups of samples of three each, each group having a different Sørensen value. To one of the samples of each group was added 5 mg. of cystine and to another 5 mg. of cysteine, the remaining sample being used as a control. The dilution of each sample with liquid was made the same by appropriate additions of water. The total dilution amounted to but 3 cc. for each 20g. sample. The samples were heated in sealed tubes for 45 minutes at 120° and then analyzed for hydrogen sulfide. The test was made on fresh flesh and on flesh which had decomposed to some extent during 24 hours' standing at room temperature. The results are shown in Table II.

TABLE II

ROCKFISH FLESH (20 G.) HEATED WITH AND WITHOUT ADDED CYSTINE OR CYSTEINE

Material	Fresh		After standing at room temperature for 24 hrs.	
	<i>P_H</i> before heating	H ₂ S after heating, mmg.	<i>P_H</i> before heating	H ₂ S after heating, mmg
Flesh alone	5.0	5	5.6	106
Flesh + 5 mg. cystine	5.0	0	5.6	204
Flesh + 5 mg. cysteine	5.0	0	5.6	231
Flesh alone	5.6	10	6.6	342
Flesh + 5 mg. cystine	5.6	0	6.6	544
Flesh + 5 mg. cysteine	5.6	0	6.6	560
Flesh alone	7.0	0	7.6	751
Flesh + 5 mg. cystine	6.8	0	7.6	1064
Flesh + 5 mg. cysteine	6.8	0	7.6	829
Flesh alone	7.8	0	8.4	1728
Flesh + 5 mg. cystine	7.8	0	8.4	2293
Flesh + 5 mg. cysteine	7.8	5	8.4	2137

Little, if any, hydrogen sulfide could be detected in the fresh samples after heating, regardless of the H-ion concentration. In the stale samples the amount of gas produced was greater the higher the *P_H* and also greater in the samples containing cystine or cysteine than in the flesh alone. In endeavoring to reach a satisfactory explanation of these results, the

author considered two possibilities. One is that neither cystine nor cysteine under these conditions decomposes to give hydrogen sulfide, the gas obtained having been derived from a thermolabile decomposition product of cystine and cysteine. The other is that these amino acids are decomposed by the heat with the direct production of hydrogen sulfide, the gas, however, being partially or wholly destroyed only in the case of the fresh flesh.

The following experiments were performed for the purpose of testing the validity of these explanations.

Decomposition of Cystine

If cystine, during its contact with the stale flesh, is changed to a thermolabile product, the longer the contact the greater the change. Accordingly, cystine was allowed to remain admixed with stale rockfish flesh for different periods before heating. The shortest period used was the minimum time required to insert the flesh in a tube, seal the tube, and place it in a hot calcium chloride brine bath. All samples were heated at 120° for 45 minutes. The results (Table III) show that the duration of contact of the cystine with the stale flesh had little influence, if any, on the amount of hydrogen sulfide produced. This tends to disprove the first hypothesis.

TABLE III

INFLUENCE OF DURATION OF CONTACT OF CYSTINE WITH SPOILED ROCKFISH FLESH (20 G.) ON THE AMOUNT OF HYDROGEN SULFIDE PRODUCED DURING HEATING OF THE MIXTURE FOR 45 MINUTES AT 120°

Material	Duration of contact, min.	Hydrogen sulfide, mmg.
Flesh alone	..	654
Flesh + 4.8 mg. cystine	3	825
Flesh + 4.8 mg. cystine	20	801
Flesh + 4.8 mg. cystine	40	836

Several experiments, the details of which it will not be necessary to describe, showed that when fresh flesh was heated, any hydrogen sulfide which may have been present was practically wholly destroyed, probably by oxidation. When stale flesh, which alone yielded large quantities of hydrogen sulfide when heated, was mixed with fresh flesh and then heated for 45 minutes at 120°, analysis revealed little or no hydrogen sulfide. Likewise, when hydrogen sulfide water was added to fresh flesh, none of the gas could be detected after heating the mixture. The gas was not lost in this way, however, when added to stale flesh.

Tillmans and Otto⁷ suggest three methods of detecting incipient decomposition of fish, all of which are based upon the reducing power of the flesh. The most delicate is an adaptation of Winkler's method⁸ for the

⁷ Tillmans and Otto, *Unters. Nahr. u. Genussm.*, 47, 25-37 (1924).

⁸ Winkler, *Ber.*, 21, 2843 (1888); 22, 1764 (1889); 24, 3602 (1891).

determination of dissolved oxygen in water. Five grams of ground flesh is placed in a Winkler bottle, distilled water is added to overflowing, the stopper is inserted, and the bottle is agitated to give a fine suspension. After incubation for one or two hours at 22°, the Winkler reagents are added and the determination of dissolved oxygen is completed. If no oxygen is present under these conditions, according to Tillmans and Otto, the product is unfit for human consumption.

That the reducing power of the flesh is quickly built up while the product is held at room temperature was shown in tests conducted by the author. The titration figures for fish flesh so held changed from about 1.0 cc. of 0.1 *N* sodium thiosulfate solution to practically nil in 18 hours. The possibility of the destruction of hydrogen sulfide by oxidation by the flesh before it has reached the reducing stage is thus explained.

The data presented thus far seem to point to the destruction of part at least of the cystine during the heating of either the fresh or the stale flesh. If heat will destroy the cystine, the destruction should be a function of the temperature. Using Sullivan's method,⁴ cystine was determined in flesh which had been heated at 100 and at 120° and to which cystine had been added prior to heating. The results showed an apparent destruction of the cystine, for the mixture (20 g. of flesh + 15 mg. of cystine) at 100° gave 18 mg. of cystine, whereas that at 120° gave only 5 mg. The flesh without cystine gave about 2 mg. of cystine after heating at 120°.

Such results, however, might be explained as being due to a combination of the cystine with other constituents of the flesh, the combining power of cystine being generally recognized. To settle this point, the cystine-flesh mixture, after heating, was hydrolyzed with 20% hydrochloric acid for six hours.⁹ Following the procedure recommended by Sullivan¹⁰ for the determination of cystine in casein, the hydrolysate was filtered, decolorized with Norit, neutralized and tested for cystine. The amount of cystine in 20 g. of the mixture before heating was 128 mg. After heating there were but 61 mg. Since only 15 mg. of cystine had been added, it is evident that some of the original combined cystine of the flesh was also destroyed by the heating. This was checked by heating flesh to which no cystine had been added. The cystine content of the hydrolysate decreased as a result of the heating from 107 mg. to 82 mg. There seems to be little doubt, therefore, that some of the cystine is destroyed during the heating of the flesh.

Summary and Conclusions

When fresh fish flesh was heated in a sealed tube at 120° for 45 minutes, either no hydrogen sulfide or only a comparatively small amount could

⁹ Sullivan, unpublished data.

¹⁰ The author acknowledges his indebtedness to Dr. M. X. Sullivan for his helpful suggestions in connection with this study.

be detected in the heated product. When the flesh had become somewhat stale, the same heat treatment yielded the gas in relatively large amounts. Added cystine increased the amount of residual hydrogen sulfide only in the case of the stale flesh. The cause of this difference in results with fresh and stale flesh was traced to the ability of the fresh flesh, and, conversely, the inability of the stale flesh, to destroy hydrogen sulfide formed by the heating. The gas is destroyed apparently by oxidation. Cystine added to fresh flesh, as well as that present in combined form in the flesh, is partially destroyed by this heating.

On the plausible assumption that the effect of processing a can of fish is the same as the effect of the above-mentioned heat treatment in a sealed tube, it may be concluded that the presence of considerable hydrogen sulfide in a canned product of this nature indicates that the raw material at the time of canning was in poor condition.

It is recognized that sulfur compounds other than cystine may exist in the protein or other constituents of the flesh examined, but the possibility of their existence therein need not be considered in connection with this study. While these results were obtained with fish flesh, which procedure had the advantage that the raw material could be obtained in fresh condition at any time desired with little inconvenience, it is probable that similar results would be obtained with other flesh products. Therefore, the conclusion seems justified that when flesh products in general are heated at temperatures above 100° some of the cystine is destroyed and hydrogen sulfide derived therefrom may be detected in the product, providing the gas is not oxidized by the material during the heating process.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF GEORGIA]
**THE BECKMANN REARRANGEMENT OF SALICYLHYDROXAMIC
ACID DERIVATIVES¹**

BY ALFRED W. SCOTT AND J. H. MOTE

RECEIVED JUNE 20, 1927

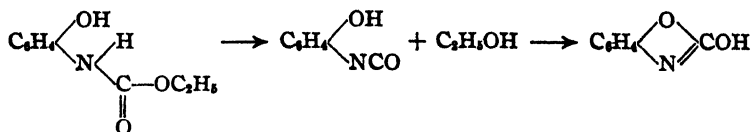
PUBLISHED OCTOBER 5, 1927

Several benzene derivatives containing an hydroxyl group and a nitrogenous group in the ortho position to each other can be converted into oxycarbanil by suitable treatment.² Especially in the cases of urea and urethan derivatives is there the possibility of the intermediate formation

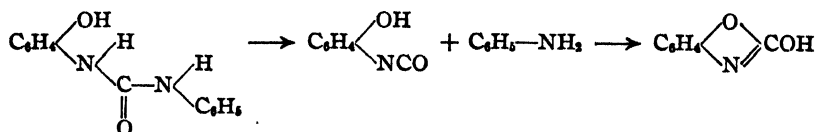
¹ This paper is based upon a thesis presented by Mr. J. H. Mote to the Graduate School of the University of Georgia, in partial fulfillment of the requirements for the degree of Master of Science.

² (a) Groenvik, *Bull. soc. chim.*, 25, 177 (1876); (b) Kalckhoff, *Ber.*, 16, 1828 (1883); (c) Leuckart, *J. prakt. Chem.*, [2] 41, 327 (1890); (d) Bender, *Ber.*, 19, 2269, 2951 (1886); (e) Sandmeyer, *Ber.*, 19, 2656 (1886); (f) Chetmicki, *Ber.*, 20, 177 (1887); (g) Jacoby, *J. prakt. Chem.*, [2] 37, 29 (1888); (h) Lellmann and Bonhöffer, *Ber.*, 20, 2126 (1888).

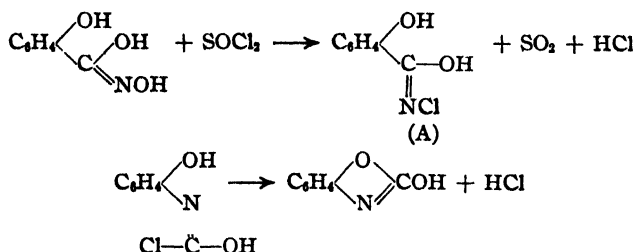
of an isocyanate, for instance, in the pyrogenic treatment of *o*-oxyphenylurethan by Groenvik^{2a} or in the decomposition of *o*-oxydiphenylurea in



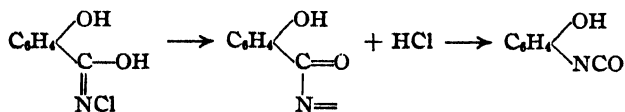
an alkaline aqueous solution by Leuckart.^{2c}



Marquis³ studied the rearrangement of salicylhydroxamic acid when it was treated with thionyl chloride. He assumed a true Beckmann rearrangement to take place and explained the formation of oxycarbanil without the intermediate formation of an isocyanate, as follows.



According to the theory advanced by Stieglitz⁴ the change of the radical from C to N would be caused by the loss of HCl from (A) and the formation of univalent nitrogen. After the interchange the compound would assume the structure of an isocyanate, as follows.



and consequently the formation of the oxycarbanil would take place from the isocyanate.

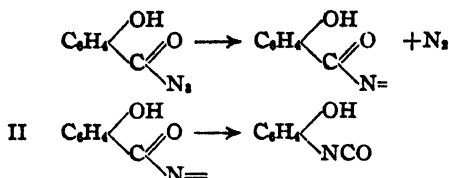
However Struve and Radenhausen⁵ in a study of the rearrangement of *o*-oxybenzazide in boiling water obtained *sym*.-di-*o*-oxyphenylurea, carbon dioxide and nitrogen. This is the Beckmann rearrangement of the Curtius type⁶ and according to the theory of the mechanism advanced by Stieglitz is assumed to proceed as follows.

² Marquis, *Compt. rend.*, **143**, 1164 (1907).

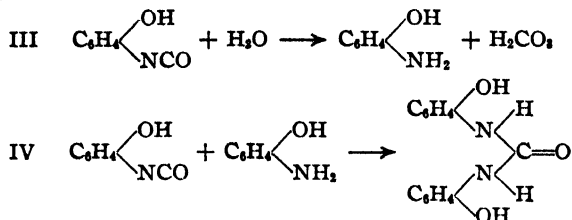
⁴ References given by Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914).

⁵ Struve and Radenhausen, *J. prakt. Chem.*, [2] **52**, 241 (1895).

⁶ Curtius and Leimbach, *ibid.*, [2] **65**, 20 (1902).



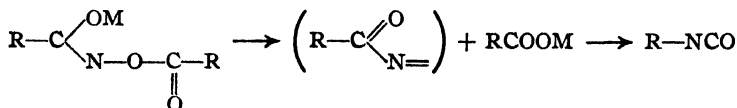
In the presence of water the isocyanate would hydrolyze to give an amine and carbonic acid. The amine would then react with some unchanged isocyanate to give a *sym.*-di-substituted urea.



In the reactions of both Marquis and of Struve and Radenhausen the same isocyanate would seem to be formed as an intermediate product in the rearrangement. However, in one instance a *sym.*-di-substituted urea resulted and in the other oxycarbanil was formed. Of course, since the experiments of Marquis were carried out in non-aqueous solution, this would account for the absence of the urea in their case and would indicate that the oxycarbanil was formed directly from the isocyanate in the absence of water. However, in the work of Leuckart^{2c} in an alkaline aqueous solution oxycarbanil was the product formed.

In view of these results, we decided to study another type of Beckmann rearrangement that should give us the same isocyanate, both in aqueous solution and in the dry state.

According to the theory of Stieglitz the alkali salts of the esters of hydroxamic acids undergo rearrangement as follows.



This isocyanate in aqueous solution would be expected to behave in accordance with Reactions III and IV given above. We studied a rearrangement of this type using the alkali salts of the acetyl and benzoyl esters of salicylhydroxamic acid. The isocyanate formed from these salts should be the same as that occurring in the cases previously discussed.

In aqueous solution oxycarbanil and an acetate or a benzoate were isolated from the mixture after rearrangement. We were unable to detect the presence of *o*-aminophenol, which would indicate the formation of *sym.*-dioxyphenylurea and its subsequent decomposition. Furthermore,

when the salts were exploded by heating, there was no trace of the characteristic odor of an isocyanate which is usually obtained when the salts of hydroxamic acid esters are decomposed by heat.

It would seem, therefore, that when the derivatives of salicylhydroxamic acid undergo the Beckmann rearrangement either in aqueous solution or in the dry state no isocyanate is formed or at least only momentarily. Oxycarbanil is formed, seemingly, either during the course of Reaction II or at least immediately upon its completion.

Experimental Part

Salicylhydroxamic Acid was prepared by the method of Jeanrenaud.⁷

The Acetyl Ester ($C_6H_4(OH)CONHOCOCH_3$) was prepared by mixing 1 g. of salicylhydroxamic acid with an excess of acetic anhydride and warming the mixture on a water-bath. The mixture became soft, then hardened. Acetic acid came off in the form of a vapor. The ester was recrystallized from alcohol and water and found to melt at 142° ; yield, 0.60 g.

Anal. Subs., 0.7200: 48.0 cc. of N (21° , 745.04 mm.). Calcd. for $C_9H_9O_4N$: N, 7.18. Found: 7.31.

The Potassium Salt of the Acetyl Ester was made by dissolving the ester in the least amount of absolute alcohol and treating the ester with alcoholic potash. The salt was precipitated on the addition of absolute ether. It was filtered off and washed with absolute alcohol and then with anhydrous ether. The salt was dried for one hour in a desiccator over concentrated sulfuric acid and was found to explode after fifteen seconds when immersed in a bath at 85° .

When the salt was exploded, we were unable to detect any odor of isocyanate, which might have been formed as an intermediate product and which is usually noticeable when hydroxamic acids are rearranged.

Rearrangement took place when the salt was dissolved in water and heated to boiling. On cooling down, oxycarbanil separated out as white needles which were recrystallized from hot water and found to melt at 139° . On acidifying the filtrate, acetic acid was set free. It was recognized by its odor. The aqueous solution from the rearrangement was diazotized and heated. We were unable to detect the presence of any pyrocatechol by the iron chloride reaction. This seems to show that there was no *o*-aminophenol present, which would indicate the formation of an urea which might subsequently change over into oxycarbanil.

The properties of the rearrangement product agreed in all respects with the oxycarbanil described in the literature.

Anal. Subs., 0.2063: 20.8 cc. of N (27° , 748.6 mm.). Calcd. for $C_6H_5O_2N$: N, 11.38. Found: 10.99.

The Benzoyl Ester ($C_6H_4(OH)CONHOCOC_6H_5$) was prepared by two methods.

(a) By the Schotten-Baumann reaction: To 1 g. of salicylhydroxamic acid was added an aqueous solution of sodium hydroxide containing 0.26 g. of sodium hydroxide (1 equiv.) and the mixture shaken until all dissolved. Then 0.92 g. of benzoyl chloride was added and the mixture thoroughly stirred to ensure thorough mixing. The flask was kept cool during the reaction.

The product was recrystallized from alcohol and water and found to melt at 153° ; yield, 0.80 g.

(b) By fusion with benzoic anhydride: Salicylhydroxamic acid (1 g.) was mixed

⁷ Jeanrenaud, *Ber.*, 22, 1270 (1889).

with an excess of benzoic anhydride and the whole warmed on a water-bath. The mixture became soft, then hardened again. Benzoic acid sublimed during the reaction. The mixture was repeatedly extracted with ligroin in order to remove all of the benzoic acid and unchanged benzoic anhydride. The ester was recrystallized from alcohol and water and found to melt at 153°; yield, 1.02 g.

Anal. Subs., 0.5639: 28.9 cc. of N (25°, 748.3 mm.). Calcd. for $C_{14}H_{11}O_4N$: N, 5.45. Found: 5.50.

The Potassium Salt of the Benzoyl Ester was prepared by the addition of the calculated quantity of alcoholic potash to the ester in absolute alcohol solution. The salt was precipitated by the addition of absolute ether.

The salt after drying for one hour over concentrated sulfuric acid was treated like the potassium salt of the acetyl ester and was found to explode after fifteen seconds when immersed in a bath at 81°. No odor of isocyanate was noticed when the substance exploded.

The salt on being dissolved in water and heated rearranged giving potassium benzoate and oxycarbanil. The potassium benzoate was recognized by causing benzoic acid to precipitate by the addition of acid to the solution. The benzoic acid after recrystallization melted at 121.5° and resembled in all respects the benzoic acid described in the literature.

Sodium Salt of Benzoyl Ester was prepared by treating the ester in absolute alcohol solution with the calculated quantity of sodium alcoholate. On the addition of absolute ether the sodium salt separated out. It decomposed on heating but gave no odor of isocyanate. In water solution it underwent rearrangement very much as the potassium salt.

Summary

The acetyl and benzoyl esters of salicylhydroxamic acid and their salts were made. Upon undergoing the Beckmann rearrangement these salts gave oxycarbanil instead of a *sym.*-di-substituted urea usually obtained under similar conditions from the alkali salts of the esters of other hydroxamic acids.

ATHENS, GEORGIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

THE REACTION OF PARA-SUBSTITUTED BENZYL CHLORIDES WITH SODIUM HYDROGEN SULFIDE

BY CHARLES BARKENBUS, ELI B. FRIEDMAN AND RAYMOND K. FLEGE

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Several years ago in connection with some work in progress at that time, there was needed some *p*-cyanobenzyl mercaptan. In attempting to prepare this compound by the action of sodium hydrogen sulfide on *p*-cyanobenzyl chloride a mixture of *p*-cyanobenzyl sulfide and *p*-cyanobenzyl disulfide was obtained instead of the mercaptan.¹ Shortly after our observation Horn² obtained the same results using *p*-nitrobenzyl chloride and found that the *p*-nitrobenzyl mercaptan was incorrectly described in the literature. Chloro-acetophenone also gives a mixture

¹ Friedman, *Thesis*, University of Kentucky, 1922.

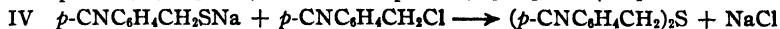
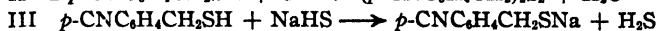
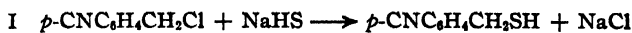
² Horn, *THIS JOURNAL*, 43, 2610 (1921).

of the corresponding sulfide and disulfide when treated with sodium hydrogen sulfide.³

Since *p*-cyanobenzyl mercaptan and its derivatives are not described in the literature it was thought advisable to study the reaction of sodium hydrogen sulfide with *p*-cyanobenzyl chloride.

In order to study this reaction it was first necessary to prepare *p*-cyanobenzyl mercaptan and the corresponding sulfide and disulfide. The mercaptan was made by hydrolyzing 2-*p*-cyanobenzylmercapto-4-methyl-6-oxypyrimidine with dilute hydrochloric acid. The sulfide and disulfide were made by the usual methods.

The following reactions will account for the formation of *p*-cyanobenzyl sulfide and disulfide.



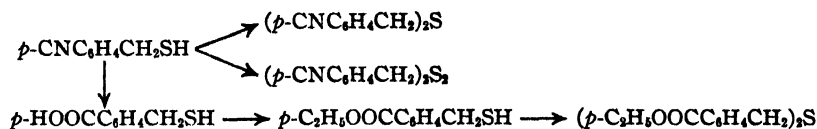
The formation of the disulfide is due to oxidation of the mercaptan and can be eliminated by carrying out the reaction in a non-oxidizing medium such as hydrogen or hydrogen sulfide. The formation of the sulfide first necessitates the formation of the sodium salt, which in turn reacts with *p*-cyanobenzyl chloride. With a slight excess of sodium hydrogen sulfide, as is generally used, the sulfide will be formed provided Reactions III and IV proceed as fast or faster than Reaction I. By adding sodium hydrogen sulfide to the reaction mixture as fast as it is used up, the mercaptan should be formed in greater amount provided the speed of Reaction I is the greatest. Only traces of the mercaptan could be obtained using this condition, which indicated that Reactions III and IV proceed as fast as Reaction I or faster. The only condition that gave enough mercaptan to isolate was when hydrogen sulfide was used as the non-oxidizing medium and sodium hydrogen sulfide was added as fast as it reacted. Other non-oxidizing media such as hydrogen gave only traces of the mercaptan. This can be explained by the retarding action of hydrogen sulfide on Reaction III. The best experimental conditions for the formation of the mercaptan are given in the experimental part, though many other runs were made using various solvents and temperatures.

In order to see what influence other groups might have, two small runs were made using *p*-carbethoxybenzyl chloride. In this case the resulting crude mercaptan and sulfide were obtained in about equal amounts. These results would indicate that the different groups in the para position affect the speeds of Reactions I, III and IV, but in varying amounts. The

³ (a) Tafel and Mauritz, *Ber.*, **23**, 3474 (1890). (b) Bertil Groth, *Arkiv. Kemi Mineral Geol.*, **9**, No. I, 63 (1924).

negative groups such as the nitro, cyano and carbethoxy seem to increase the speeds of Reactions III and IV, though not to the same extent. The positive chlorine in the para position, on the other hand, does not seem to increase the speeds of Reactions III and IV, since *p*-chlorobenzyl mercaptan has been made by treating *p*-chlorobenzyl chloride with potassium hydrogen sulfide and no mention was made of sulfide formation.⁴

During the course of these experiments the following compounds were made, as shown by the diagram.



p-Carboxybenzyl mercaptan could not be made from *p*-carboxybenzyl chloride by treating with sodium hydrogen sulfide since the sodium salt of this acid reacts with itself to give a complex ester.⁵ Attempts to prepare the sulfide or disulfide of *p*-carboxybenzyl mercaptan directly from it or by hydrolysis of the corresponding cyano or carbethoxy compounds always resulted in amorphous, white compounds having no definite melting point and insoluble in all solvents. The *p*-cyanobenzyl disulfide is light yellow, which may be due to partial dissociation into the free radicals.⁶

Experimental Part

2-*p*-Cyanobenzylmercapto-4-methyl-6-oxypyrimidine.—To 750 cc. of absolute alcohol were added 12.14 g. of sodium and 75 g. of 2-thio-4-methyl-6-oxypyrimidine. The mixture was stirred vigorously while being heated for two hours in a boiling water-bath. To the resulting sodium salt was added 80.4 g. of *p*-cyanobenzyl chloride and the heating and stirring were continued until the reaction mixture was neutral. On cooling, the white amorphous solid was filtered off, washed well with water and dried at 110° for 12 hours; weight, 133 g. The crude product was crystallized from glacial acetic acid in white, microscopic plates, m. p. 240–241°; yield 110 g. or 86.5%.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{ON}_2\text{S}$: N, 16.34. Found: 16.27, 16.28.

***p*-Cyanobenzyl Mercaptan.**—One hundred and fifty g. of 2-*p*-cyanobenzylmercapto-4-methyl-6-oxypyrimidine and 1500 cc. of 6 *N* hydrochloric acid were heated to boiling with stirring for one hour. The solid pyrimidine gradually became oily and finally a thick oil remained. The mixture on cooling was extracted with ether, the ether layer washed with dilute sodium carbonate solution and water and then dried over anhydrous sodium sulfate. On distilling off the ether 82 g. of crude oil were obtained, which distilled at 135–138° at 7 mm. The oil solidified on cooling to a white crystalline mass having the characteristic garlic odor, m. p. 37°; yield 75 g. or 86.2%. It gave a white precipitate with alcoholic mercuric nitrate.

Anal. Calcd. for $\text{C}_7\text{H}_7\text{NS}$: S, 21.47. Found: 20.63, 20.79.

***p*-Cyanobenzyl Sulfide.**—The calculated amount of sodium was added to 100 cc.

⁴ Jackson and White, *Am. Chem. Jour.*, **2**, 167 (1880).

⁵ Barkenbus and Holtzclaw, *THIS JOURNAL*, **47**, 2189 (1925).

⁶ Lecher, *Ber.*, **48**, 524, 1425 (1915).

of absolute alcohol and to this solution were added 5 g. of *p*-cyanobenzyl mercaptan and 5 g. of *p*-cyanobenzyl chloride. The mixture was refluxed for four hours until neutral. The alcohol was evaporated off and the crude solid shaken up with water, filtered and crystallized from 95% alcohol, giving fine, white, odorless needles; m. p. 115°; yield 6 g. or 67.7%.

Anal. Calcd. for $C_{10}H_{12}N_2S$: N, 10.61. Found: 10.47, 10.48.

***p*-Cyanobenzyl Disulfide.**—Five g. of *p*-cyanobenzyl mercaptan was dissolved in 100 cc. of 95% alcohol and 25 cc. of concentrated ammonium hydroxide added. After standing exposed to the air for four days a light yellow, crystalline solid came out and was crystallized from 95% alcohol giving light yellow, odorless, flat needles; m. p. 148°; yield 3.5 g. or 70.4%.

Anal. Calcd. for $C_{10}H_{12}N_2S_2$: N, 9.46. Found: 9.32.

Reaction of Sodium Hydrogen Sulfide with *p*-Cyanobenzyl Chloride.—Fifty g of *p*-cyanobenzyl chloride was dissolved in 400 cc. of absolute alcohol and to this solution was added an absolute alcohol solution of sodium hydrogen sulfide made by saturating a sodium ethylate solution with hydrogen sulfide. A fast stream of hydrogen sulfide was passed into the boiling alcohol solution during the experiment. The sodium hydrogen sulfide solution was added very slowly while the mixture was stirred vigorously and the reaction mixture was tested every minute for alkalinity with methyl red. At no time was it alkaline until the calculated amount of sodium hydrogen sulfide had been added, indicating that the reaction took place as fast as it was added. As soon as the reaction mixture became alkaline, it was made slightly acid with hydrochloric acid and allowed to stand overnight in an atmosphere of hydrogen sulfide. A large amount of light yellow needles separated out. These were filtered off with suction, washed well with alcohol and then suspended in water to dissolve the sodium chloride. They were again filtered, washed well with water and dried at 100° for twelve hours. On crystallizing from 95% alcohol, long white needles were obtained, m. p. 115°, which indicated the sulfide.

The alcoholic filtrate was evaporated in a stream of hydrogen and a reddish oil mixed with some salt was left. The oil was taken up in ether, dried over anhydrous sodium sulfate and distilled. Eleven g. of crude oil was obtained, which on redistillation gave 5 g. of *p*-cyanobenzyl mercaptan; m. p. 32°; yield 10.2%; yield of *p*-cyanobenzyl sulfide, 34 g. or 78.2%. This was the best yield obtained of the mercaptan out of many different runs.

Reaction of Sodium Hydrogen Sulfide with *p*-Carbethoxybenzyl Chloride.—The calculated amount of alcoholic sodium hydrogen sulfide solution was added very slowly to a boiling solution of 35 g. of *p*-carbethoxybenzyl chloride in 175 cc of absolute alcohol. Sodium chloride precipitated out immediately, and the reaction mixture did not become alkaline until all of the sodium hydrogen sulfide solution had been added. It was then made slightly acid and poured into five volumes of water. An oil separated out which was taken up in ether and dried over anhydrous sodium sulfate. On evaporating the ether, 33 g. of crude oil remained, which on distilling yielded 19.7 g. of a clear oil with a garlic odor; b. p. 135–160° at 8 mm. The oil, even on redistilling, was impure, as shown by analysis, but it was identified as *p*-carbethoxybenzyl mercaptan by converting some of it into the sulfide. The residue from the original distillation was taken up in 95% alcohol, decolorized with carbon, and allowed to crystallize, giving long white asbestos-like needles; m. p. 78°; yield 9 g. Analysis showed this to be *p*-carbethoxybenzyl sulfide.

Anal. Calcd. for $C_{10}H_{12}O_4S$: S, 8.93. Found: 9.22, 9.16.

***p*-Carboxybenzyl Mercaptan.**—Five g. of *p*-cyanobenzyl mercaptan and 150 cc. of

concentrated hydrochloric acid were heated to boiling with vigorous stirring for three hours. A white solid separated out which was filtered off, dissolved in dilute sodium carbonate solution and then filtered from a small amount of insoluble material. On acidification a white, amorphous solid was obtained which was crystallized from 95% alcohol, giving white microscopic needles with only a faint odor; m. p. 176° ; yield 5 g. or 89.3%.

Anal. Calcd. for $C_8H_8O_2S$: S, 18.89. Found: 18.41, 18.50

***p*-Carbethoxybenzyl Mercaptan.**—Twenty-two g. of *p*-carboxybenzyl mercaptan was dissolved in 200 cc. of absolute alcohol which had been previously saturated with dry hydrogen chloride gas and the mixture heated under a reflux condenser for twelve hours. The resulting solution was filtered from a small amount of insoluble material, evaporated to 100 cc. and then poured into 500 cc. of water. The oil which separated was dissolved in ether, the ether solution washed free from acid and then dried over anhydrous sodium sulfate. After evaporating off the ether the remaining oil was distilled to a colorless and nearly odorless oil; b. p. $140-141^{\circ}$ at 6 mm.; yield 19.1 g. or 74.2%.

Anal. Calcd. for $C_{10}H_{12}O_2S$: S, 16.32. Found: 16.15, 16.29.

***p*-Carbethoxybenzyl Sulfide.**—The calculated amount of freshly prepared alcoholic sodium sulfide solution was slowly added with rapid stirring to a boiling solution of 5 g. of *p*-carbethoxybenzyl chloride in 100 cc. of alcohol. When all the sodium sulfide solution had been added, the mixture was cooled and diluted with water. The white precipitate was filtered off and crystallized from alcohol producing white, asbestos-like needles; m. p. 78° ; yield 3.5 g. or 77.7%. A mixture of this compound with the product obtained by the reaction of *p*-carbethoxybenzyl chloride with sodium hydrogen sulfide had the same melting point.

Summary

The reaction of *p*-cyanobenzyl chloride with sodium hydrogen sulfide has been studied, and a mixture of *p*-cyanobenzyl sulfide and disulfide was obtained instead of the mercaptan. If a non-oxidizing atmosphere is used, only a very small amount of *p*-cyanobenzyl mercaptan is formed, the main product being the sulfide. Negative groups such as the nitro, cyano and carbethoxy in the para position of substituted benzyl chlorides favor the formation of the sulfide, while the positive chlorine favors the formation of the mercaptan.

p-Cyanobenzyl mercaptan, *p*-carboxybenzyl mercaptan, *p*-carbethoxybenzyl mercaptan, *p*-cyanobenzyl sulfide, *p*-cyanobenzyl disulfide and *p*-carbethoxybenzyl sulfide have been prepared and described.

LEXINGTON, KENTUCKY

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

CONTRIBUTION TO THE THEORY OF ACID AND BASIC CATALYSIS. THE MUTAROTATION OF GLUCOSE

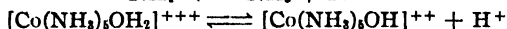
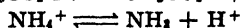
BY J. N. BRÖNSTED AND E. A. GUGGENHEIM

RECEIVED JULY 15, 1927

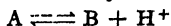
PUBLISHED OCTOBER 5, 1927

1. Introduction. The Conception of Acids and Bases

According to an extended conception of acids and bases,¹ a molecule, whether neutral or electrically charged, is defined as being an acid if it has a tendency to split off a hydrogen nucleus and as being a base if it has a tendency to unite with a hydrogen nucleus. If we compare the balanced reactions



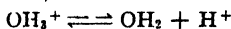
the fact that some of the molecules are neutral and others electrically charged is trivial in comparison with the fundamental similarity of the three equilibria. In general we may write the acid-base equilibria as



where A is an acid and B the conjugate base; A and B may have any electrical charge, positive, zero or negative, but naturally that of the acid A is always one greater algebraically than that of the conjugate base B. It is of course possible for a molecule to be both an acid and a base; an obvious example is OH_2 which is an acid according to the scheme



the conjugate base being OH^- , whereas it is a base according to the scheme



the conjugate acid being OH_3^+ , the form in which the so-called hydrogen ion is present in aqueous solution; we shall always call OH_3^+ "oxonium" when we wish to distinguish it sharply from H^+ which we shall then call "proton."

We accordingly see that basic properties are common to all molecules tending to combine with a proton and hydroxyl is in no way unique except for the fact that in aqueous solution its conjugate acid is the solvent molecule. Similarly, since the proton does not exist in solution, the so-called "hydrogen ions" are different chemical molecules in different solvents and these various solvated hydrogen ions are in no way different from other acid molecules, except for the fact that the conjugate bases are the solvent molecules.

We shall not in the present paper enter into the important question of a general measure of the strength of acids and bases² and its dependence

¹ (a) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); (b) *J. Phys. Chem.*, **30**, 777 (1926).

² See Brönsted, *Om Syre-og Basekatalyse*, *Festschrift*, Københavns Universitet, 1926.

on the solvent. In dilute aqueous solution, however, at a given temperature the strength of an acid A might be measured by the equilibrium constant K_A' of the process defining the acid; that is, K_A' is the limiting value at infinite dilution of the ratio $c_B \cdot c_{H^+} / c_A$ in which c_B , c_{H^+} and c_A are equilibrium values of the concentrations of B, H^+ and A, respectively. Owing to the fact that c_{H^+} is practically infinitesimal, K_A' is a purely formal quantity whose absolute value is too small to be measured. We can, however, also quite formally attribute an equilibrium constant K° to the process defining the acid property of oxonium ion; thus $K^\circ = c_{OH_2} \cdot c_{H^+} / c_{OH_3^+}$ where c_{OH_2} , c_{H^+} and $c_{OH_3^+}$ are equilibrium values of the concentrations of OH_2 , H^+ and OH_3^+ , respectively. Then the strength of the acid A relative to oxonium may be measured by the ratio K_A' / K° or $c_B \cdot c_{OH_2} / c_A \cdot c_{OH_3^+}$, which is the mass action constant of the actual double acid-base equilibrium in the solution. But as in dilute aqueous solution c_{OH_2} is constant we can equally well measure the relative strength of an acid A by the ratio $c_B \cdot c_{OH_3^+} / c_A$. This we shall call the acid constant and denote it by K_A . We shall find it convenient to measure the strength of the conjugate base B by the reciprocal of K_A ; this we shall call the basic constant of B and denote it by K_B .

For such an acid as acetic acid, K_A is identical with the ordinary electrical dissociation constant in water $c_{Ac^-} \cdot c_{OH_3^+} = c_{AcH}$. For such an acid as ammonium ion we have

$$K_A = \frac{c_{NH_3} \cdot c_{OH_3^+}}{c_{NH_4^+}} = c_{OH_2} \cdot c_{OH^-} \cdot \frac{c_{NH_3}}{c_{NH_4^+} \cdot c_{OH^-}}$$

which is usually called the hydrolysis constant of the ammonium ion. For water we have

$$K_A = \frac{c_{OH^-} \cdot c_{OH_3^+}}{c_{OH_2}} = \frac{K_W}{55.6}$$

where $K_W = c_{OH^-} \cdot c_{OH_3^+}$, the usual dissociation constant of water, and for oxonium ion

$$K_A = \frac{c_{OH_2} \cdot c_{OH_3^+}}{c_{OH_3^+}} = c_{OH_2} = 55.6$$

For a "strong" acid, such as hydrochloric acid, K_A is immeasurably great and for a hydrocarbon it is so small that one would generally say that a hydrocarbon is not an acid at all.

2. Catalysis by Acids and Bases

It is a well-known and striking fact that a considerable number of reactions in aqueous solution can be accelerated by increasing the concentration of hydrogen ion, that of hydroxyl ion or that of either. In most cases that have been carefully studied it is found that the increase in reaction rate is at least approximately proportional to the concentration of hydrogen ion or hydroxyl ion, as the case may be. That is to say, the velocity constant k of the reaction is given by

$$k = k_0 + k_{\text{OH}_3^+} \cdot c_{\text{OH}_3^+} + k_{\text{OH}^-} \cdot c_{\text{OH}^-}$$

where k_0 , $k_{\text{OH}_3^+}$ and k_{OH^-} are at each temperature constants for the reaction, while $c_{\text{OH}_3^+}$ and c_{OH^-} are the concentrations of hydrogen ion and hydroxyl ion, respectively; any of the constants k_0 , $k_{\text{OH}_3^+}$ or k_{OH^-} may be negligibly small or zero.

According to our present point of view the hydrogen and hydroxyl ions are not unique as the carriers of acid and basic properties; there is, however, no *a priori* reason to expect that the position they hold as catalysts is unique. On the contrary, one would expect that other acid and basic molecules should act as catalysts as well. The available experimental data do not disagree with this theory of more general acid and basic catalytic effects because in most actual cases the conditions of the experiments have been such that the effects of other catalysts would have been masked by those of OH_3^+ and OH^- . In the few cases where this is not so, "anomalies" in the catalytic actions are detectable³ for which our present suggestion seems to furnish a reasonable explanation.

This theory has already been verified in this Laboratory for the basic catalysis of the decomposition of nitramide.⁴ Dawson and Carter's more recent experiments⁵ on the reaction between acetone and iodine also show that this reaction is catalyzed not only by hydroxyl and oxonium ions but also by the anions and undissociated molecules of weak acids. In the solutions used by them, however, the effects of the various catalysts are difficult to separate and we cannot agree with their computations, which involve a confusion between concentration and activity.

The investigations on nitramide have shown that this substance decomposes slowly in aqueous solution at a rate unaffected by neutral salts at small concentration and by strong acids, provided the solution is at least slightly acid, but is decomposed very rapidly in alkaline solution; in other words, the reaction is not affected by oxonium, but is strongly catalyzed by hydroxyl ions. The decomposition has been studied in buffer solutions of the type acetic acid-sodium acetate and also in buffer solutions of the type aniline-anilinium chloride, the solutions being in all cases sufficiently dilute so that the salt effect could be neglected and sufficiently acid so that the effect of hydroxyl could be neglected. Any acceleration observed could thus only be due to the constituents of the buffer. The results obtained showed that there was a pronounced effect proportional to the concentration of the basic constituent of the buffer and independent of the acid constituent. This can be expressed by the formula

$$k = k_0 + k_B c_B$$

³ Kuhn and Jacob, *Z. physik. Chem.*, 113, 389 (1924).

⁴ (a) Brönsted and Pedersen, *ibid.*, 108, 185 (1924); (b) Brönsted and Duus, *ibid.*, 117, 299 (1925).

⁵ Dawson and Carter, *J. Chem. Soc.*, 1926, 2282.

where c_B is the concentration of the base and k_b a constant characteristic of the base.

Similarly, if a reaction is catalyzed by OH_3^+ we should expect it also to be accelerated by other acids such as the undissociated molecule of formic acid. It should be mentioned that this effect would be that postulated in the so-called "dual theory of catalysis."⁶ This theory was put forward owing to a misunderstanding of salt effect, now explained, on the basis of the theory of the complete dissociation of strong electrolytes,⁷ and has little in common with our present point of view.

3. The Salt Effect

So far in our discussion we have made no distinction between activity and concentration; in other words we have ignored salt effect, and we must now consider briefly what part it plays in catalysis.

According to the theory of reaction rate in dilute solution,⁸ which has now been confirmed experimentally in a number of cases,⁹ the velocity of a reaction between X and Y is given in dilute solution by the expression $k c_X c_Y f_X f_Y / f_{XY}$, where k is a constant for a given solvent and temperature, c_X and c_Y are the concentrations of the reactants, f_X , f_Y and f_{XY} are the activity coefficients of the molecular species X, Y and a complex XY, respectively. The addition of a neutral salt may affect the reaction rate in two ways. First, it may alter the factor $f_X f_Y / f_{XY}$; this is termed primary salt effect. Most catalytic reactions fall in the class where one of the reactants, say X, is uncharged, in which case the complex XY has the same charge as Y and so both f_X and f_Y / f_{XY} differ but little from unity; the factor $f_X f_Y / f_{XY}$ then varies but slightly and linearly with the concentration. Available data show that when only one of the reactants is charged, the primary salt effect is at the most 10% in decimolal solution and is usually much less. Secondly, addition of salt may affect the actual concentration c_X or c_Y of either reactant by causing a shift in an equilibrium involving X or Y; for example, if one of the reactants is hydroxyl ion in a buffer solution the addition of neutral salt may alter its concentration by shifting the buffer equilibrium. This is called secondary salt effect. It is often

⁶ (a) Acree and Johnson, *Am. Chem. J.*, **37**, 410 (1907); (b) *ibid.*, **38**, 258 (1907). (c) Senter, *J. Chem. Soc.*, **91**, 460 (1907). (d) Lapworth, *ibid.*, **97**, 19 (1910). (e) Taylor, *Z. Elektrochem.*, **20**, 201 (1914). (f) Dawson and Powis, *J. Chem. Soc.*, **103**, 2135 (1913). (g) Dawson and Reiman, *ibid.*, **107**, 1426 (1915).

⁷ Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

⁸ (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) *ibid.*, **115**, 337 (1925). (c) Bjerrum, *ibid.*, **108**, 82 (1923); (d) *ibid.*, **118**, 251 (1925).

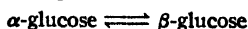
⁹ (a) Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924). (b) Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925). (c) Brönsted and King, *THIS JOURNAL*, **47**, 2523 (1925). (d) Bray and Livingston, *ibid.*, **45**, 1251 (1923). (e) Livingston and Bray, *ibid.*, **45**, 2048 (1923). (f) Kilpatrick, *ibid.*, **48**, 2091 (1926). (g) Harned, *ibid.*, **49**, 1 (1927). (h) Brönsted and Livingston, *ibid.*, **49**, 435 (1927).

possible, by choosing one's solutions judiciously, to avoid secondary salt effect in studying catalysis and this should for preference be done whenever it is desired to measure the effect of a definite catalyst.

4. The Mutarotation of Glucose

From the standpoint of the present theory the probability of an appreciable catalysis by ordinary acid and basic molecules in aqueous solution involves the presence of a marked effect by OH_3^+ and OH^- . In other words, the reaction to be investigated should be very sensitive to these two ions in order that the effect of weaker acids and bases may be detectable. The mutarotation of glucose fulfils these conditions of sensitivity.

The rather numerous researches on this reaction have been ably reviewed by Hudson¹⁰ and again by Kuhn and Jacob³ and therefore need not be considered in detail. It has been established that the process known as the mutarotation of glucose is a balanced one,¹¹



If k_α and k_β are the velocity constants of the two opposed processes, then equilibrium is approached according to the usual exponential law of a unimolecular process with the constant $k_\alpha + k_\beta$ the same from whichever direction the equilibrium state is approached. The constant whose value is always given in the literature is not $k_\alpha + k_\beta$ but $(k_\alpha + k_\beta) \log_{10} e$; to facilitate comparison we shall from now onward also use this constant and denote it by k .

In aqueous solutions k is given at least approximately by a formula of the type¹²

$$k = k_0 + k_{\text{OH}_3^+} c_{\text{OH}_3^+} + k_{\text{OH}^-} c_{\text{OH}^-}$$

where $c_{\text{OH}_3^+}$ and c_{OH^-} are the concentrations of hydrogen and hydroxyl ion, respectively, while k_0 , $k_{\text{OH}_3^+}$ and k_{OH^-} depend only on the temperature.

For the temperature 25° Hudson¹² gives the values $k_0 = 0.0096$, $k_{\text{OH}_3^+} = 0.258$ and $k_{\text{OH}^-} = 9750$, but we shall find that the value for k_{OH^-} is much more uncertain than the other two. Assuming, however, that these values are all of the correct order of magnitude, we see that there is quite a long range of P_H over which k does not differ appreciably from k_0 . The actual extent of this range of minimum velocity varies but slightly with the temperature, and between 15 and 30° it is from about $P_H = 4$ to $P_H = 6$.¹³ Provided then that apart from OH_2 , OH_3^+ and OH^- there are

¹⁰ Hudson, *THIS JOURNAL*, **32**, 889 (1910).

¹¹ That the mutarotation of sugars is a balanced reaction was first suggested by Lowry, *J. Chem. Soc.*, **75**, 212 (1899). It was verified experimentally for lactose by Hudson, *Z. physik. Chem.*, **44**, 487 (1903) and shortly after for glucose by Lowry, *J. Chem. Soc.*, **83**, 1314 (1903).

¹² Hudson, *THIS JOURNAL*, **29**, 1571 (1907).

¹³ Nelson and Beegle, *ibid.*, **41**, 559 (1919).

no catalysts present, k_0 is the minimum obtainable value of k . The reaction which is determined by k_0 , we shall call the "spontaneous reaction." It is easy to obtain reliable values for k_0 by using water containing a mere trace of acid; water saturated with the carbon dioxide from the air is probably sufficiently acid to give the minimum value of k . Hudson and Dale¹⁴ have collected and compared the values obtained by Hudson and others for k_0 at various temperatures; the agreement with the Arrhenius formula for temperature effect is excellent. The intrapolated value for 18° is 0.0052, while our own experiments give 0.00530.

$k_{\text{OH}_3^+}$ is determined most simply by measuring k in solutions of a strong monobasic acid of concentrations up to tenth or twentieth molal; assuming that the acid is completely dissociated, an assumption which for such dilute solutions gives an error certainly much less than the experimental one of 1 or 2%, the concentration of OH_3^+ is simply the stoichiometric concentration of the acid. If k is then plotted against this concentration, a straight line is obtained whose intercept on the k axis is k_0 and whose slope is $k_{\text{OH}_3^+}$. Hudson and Dale¹⁴ have in this way determined $k_{\text{OH}_3^+}$ at 25 and 30°. By extrapolation according to the Arrhenius formula the value for 18° is 0.13, while Meyer,¹⁵ on the basis of less accurate experiments, finds 0.124 and our own experiments give 0.145. Andrews and Worley¹⁶ in a recent paper state that they have confirmed Hudson's value for $k_{\text{OH}_3^+}$ at 25°. Their results are, however, given in terms of an unusual concentration scale and it seems probable that there has been some error in computing the concentrations, for their published data correspond to a value of 0.15 for $k_{\text{OH}_3^+}$ as compared with Hudson's value 0.26, while they find the same value, 0.0096, as Hudson for k_0 .

From the fact that good straight lines are obtained it follows that primary salt effect is undetectable in these dilute solutions. We have confirmed this in solutions containing, as well as the strong acid, various neutral salts up to an ionic strength of 0.1.

As far as hydrogen-ion catalysis is concerned, Hudson's experiments are still the clearest to interpret, the simplest to compute from and quite as accurate as any later ones. Most modern workers have, however, preferred to define their solutions by using the hydrogen electrode.^{3,17} This immediately introduces several unnecessary complications. First, there is the inevitable uncertainty of the liquid-junction e.m.f.; it is under the most favorable conditions doubtful to what extent this can be neglected; Scatchard¹⁸ has shown, moreover, that the presence of sucrose has a marked effect on its value and it is extremely probable that glu-

¹⁴ Hudson and Dale, *THIS JOURNAL*, **39**, 320 (1917).

¹⁵ Meyer, *Z. physik. Chem.*, **62**, 68 (1908).

¹⁶ Andrews and Worley, *J. Phys. Chem.*, **31**, 882 (1927).

¹⁷ Euler, Ölander and Rudberg, *Z. anorg. Chem.*, **146**, 45 (1925).

¹⁸ Scatchard, *THIS JOURNAL*, **48**, 2026 (1926).

cose, if present, will act similarly. Secondly, even if one succeeds in eliminating the liquid-junction e.m.f., the hydrogen electrode measures the activity of the hydrogen ion and not its concentration, which in dilute solutions determines the reaction rate. The situation becomes still more involved when the e.m.f. measurements are performed at a different temperature from that of the reaction velocity measurements, as has been done by Euler.¹⁷ A similar criticism applies to Nelson and Beegle's¹⁸ measurements of hydrogen-ion concentration by a combination of indicator and e.m.f. measurements, as the salt effect on the dissociation equilibrium of the indicator is a complicating factor which cannot be neglected. All these complications are, however, due to an injudicious use of the hydrogen electrode or an indicator in a case where it is much simpler and more accurate to use dilute solutions of a strong monobasic acid and equate the stoichiometric concentration of acid with the hydrogen-ion concentration, as done by Hudson.

As regards the effect of the hydroxyl ion, the situation is very different; the order of magnitude of k_{OH^-} is 10^4 and the reaction is immeasurably fast at a P_H greater than 9. It is therefore essential to work in buffer solutions, and we are at once disturbed by numerous difficulties when we try to determine the concentration of hydroxyl ion. Most modern workers have used the hydrogen electrode;^{3,17} one is thus faced with all the various complications mentioned before and in addition there is our ignorance of the value of the product $\epsilon_{OH_3^+} \cdot \epsilon_{OH^-}$ in more or less complicated salt solutions. In other words, one has to make assumptions about the activity coefficients of OH_3^+ and OH^- in the buffer solutions; this being so, one might as well assume reasonable values for activity coefficients from the beginning and calculate the hydroxyl-ion concentration directly from the composition of the buffer solution. By this method one introduces no new uncertainties and one does avoid that of the liquid-junction potential. Now most of the data are for buffer solutions containing carbonates, phosphates, citrates or other multivalent ions of which our knowledge of activity coefficients is rather meager. One exception is the experiments of Osaka¹⁹ performed at 25° in solutions containing mixtures of ammonia and ammonium chloride. Now the activity coefficients of HCl, KOH and the various alkaline chlorides, as given by Scatchard,²⁰ are probably accurate to 1% and at concentrations below 0.07 *M* they all agree to within 4%. We can, therefore, choose values for the activity coefficient of any univalent ion, in solutions containing no ions of higher charge, which are probably accurate to about 2%. The presence of glucose in the solution will presumably alter these values somewhat, but as we know nothing of the magnitude of this effect we must neglect

¹⁹ Osaka, *Z. physik. Chem.*, **35**, 661 (1900).

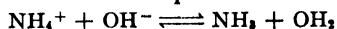
²⁰ Scatchard, *THIS JOURNAL*, **47**, 648 (1925).

it; this procedure would still be necessary in order to calculate hydrogen- or hydroxyl-ion concentration even if it were possible to measure hydrogen-ion activity accurately. The following table shows the results obtained from Osaka's experiments. The first two columns give the concentrations

TABLE I
OSAKA'S EXPERIMENTS WITH AMMONIA-AMMONIUM ION BUFFER SOLUTIONS ($t = 25^\circ$)

$\frac{c_{\text{NH}_4\text{Cl}}}{\times 10^2}$	$\frac{c_{\text{NH}_3}}{\times 10^2}$	f_1	$\frac{K_{\text{NH}_3}}{f_1^2} \times 10^5$	$c_{\text{OH}^-} \times 10^5$	$k \times 10^3$	$\frac{(k - k_0)}{\times 10^2} \frac{k - k_0}{c_{\text{OH}^-}} \times 10^{-4}$
6.67	4.42	0.80	2.83	1.87	3.60	2.64
5.00	3.32	.815	2.72	1.81	3.35	2.39
2.25	2.14	.865	2.42	2.30	3.26	2.30
2.25	3.22	.865	2.42	3.46	3.82	2.86
3.33	4.42	.845	2.54	3.37	4.46	3.50
2.25	4.27	.865	2.42	4.59	4.94	3.98
2.25	5.35	.865	2.42	5.75	6.40	5.44
2.25	6.41	.865	2.42	6.90	7.05	6.09

of NH_4Cl and NH_3 , respectively; the third gives the value assumed for f_1 , the activity coefficient of a univalent ion at the corresponding concentration of NH_4Cl . Now from the equilibrium



we have

$$c_{\text{OH}^-} = \frac{c_{\text{NH}_3}}{c_{\text{NH}_4^+}} \frac{K_{\text{NH}_3}}{f_1^2}$$

where K_{NH_3} is the dissociation constant of NH_3 at zero salt concentration. The value assumed for K_{NH_3} at 25° is 1.81×10^{-5} .²¹ The fourth column gives values of K_{NH_3}/f_1^2 and the fifth those of c_{OH^-} calculated from this equation. The sixth column gives the values observed for k . If we assume that in these solutions the hydroxyl ion is the only cause of the variation in the velocity constant we should have an equation of the form

$$k = k_0 + k_{\text{OH}^-} c_{\text{OH}^-}$$

The value 0.0096 for k_0 at 25° found by Hudson¹² has been confirmed recently by the very careful experiments of Worley and Andrews.²² In the seventh column are given values of $(k - k_0)/c_{\text{OH}^-}$ or k_{OH^-} calculated from this value of k_0 . A glance at these values shows that there is an uncertainty of 50% in the value 9750 for k_{OH^-} computed by Hudson from the same data. It is noticeable that the two values of $(k - k_0)/c_{\text{OH}^-}$ that differ markedly from the remainder correspond to solutions of markedly higher salt concentration; it should, therefore, be emphasized that if we had not introduced the factor $1/f_1^2$ to account for secondary salt effect, the deviations in these cases would have been over 12% greater than they appear now. After discussing the results of our own experiments, we shall reconsider these deviations in the light of a possible catalytic effect of the NH_3 molecule.

²¹ Noyes and Kanolt, *Carnegie Inst. Wash. Pub.*, **63**, 285 (1907).

²² Worley and Andrews, *J. Phys. Chem.*, **31**, 742 (1927).

It has been established that the same unimolecular constant is obtained for the mutarotation of glucose whether the progress of the reaction be measured by the optical rotation, the usual method, or by the refractive index or by the volume of the solution.²³ There is, moreover, little to choose between the three methods as far as accuracy is concerned.

5. Experimental Method and Method of Calculation

The method used by us was the dilatometric. The apparatus is shown in Figure 1. A is the mixing chamber fitted with a mechanical stirrer, a thermometer graduated in fiftieths of a degree centigrade and a quartz-platinum resistance thermometer used as

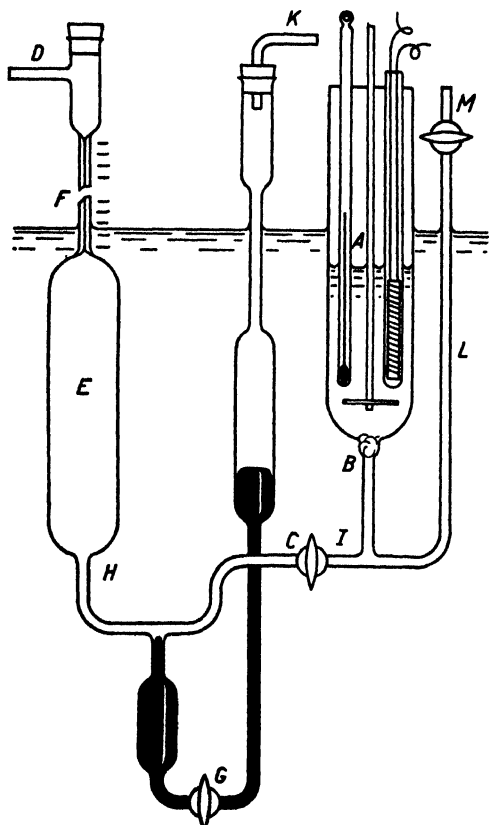


Fig. 1.

graph rose to H; the stopcock C was opened again so that mercury flowed up through C as far as I, when C was quickly closed. Finally, a slight suction was applied to K so as to bring the surface of the solution to a convenient level in the capillary F, and G was closed. The whole operation from the time the glucose was added took about seven minutes. The progress of the reaction was then followed by watching

a heating coil. At B was placed a plug of cotton wool. All three stopcocks being closed, the solution was placed in the mixing chamber and stirred; after it had attained the temperature of the thermostat, the thermometer reading was noted. The solution was then heated through rather more than 1° by means of the heating coil and the glucose (18 g. to 180 cc. of solution) was dropped in. It dissolved very rapidly and the temperature fell slightly below its original value. By carefully switching the current on and off it was possible to get the solution to its initial temperature correct to 0.01° within two minutes of dropping in the glucose. The stirrer, thermometer and heating coil were removed and A was closed with a rubber stopper through which passed a glass tube connected to a water pump. Suction was applied for about one minute to remove air bubbles. The stopcock C was then opened and by evacuating through D the solution was drawn up into the dilatometer E as far as the top of the capillary F when C was closed. The stopcock G was then opened so that the mercury filling that part of the apparatus shaded in the diagram

²³ (a) Pratolongo, *Rend. ist. lombardo Sci.*, (2), **45**, 961 (1912); (b) Riiber, *Ber.*, **55**, 3132 (1922); (c) **56**, 2185 (1923); (d) **57**, 1599 (1924).

the rise of the meniscus in the capillary; readings were taken with a magnifying glass viewed through a horizontal tube about 5 cm. in length so as to reduce the parallax. The capillary was graduated in millimeters and readings were recorded to 0.05 mm., the error probably being less than 0.1 mm. The graduation of the capillary was calibrated by noting the apparent length of a weighed thread of mercury at different places. It was found that the cross section of the capillary was about 0.60 mm. The scale graduations were uniform with an accuracy of $\pm 1\%$ throughout, but over a range of 70 mm. they were uniform with an accuracy of $\pm 0.25\%$ and only this part of the capillary was used.

Since the change in volume in this reaction is exceptionally small, it was of the greatest importance that there should be no leakage during a reaction. In a number of preliminary experiments in different apparatus, in which mercury was not used to confine the solution, it was found very difficult to keep the tap corresponding to C tight. Although this tap was freshly greased before each experiment, small leaks of the order of a cubic millimeter in several hours were apt to develop. When, however, the solution was confined in the dilatometer by the mercury column it was possible to make five to ten experiments before any leak was detectable and it became necessary to regrease C. The tightness of the stopcock C was easily tested before and after an experiment by applying strong suction to A and watching the meniscus of the liquid in F. An experiment was always rejected if a leak, however slight, was detected. In the reaction diacetone alcohol \rightarrow acetone, also studied in a dilatometer first by Koelichen²⁴ and recently by Åkerlöf²⁵ such small leaks as those described above would be of no significance. The apparatus was emptied by opening the stopcock M and sucking the solution through L. The capillary F of the dilatometer was cleaned with chromic acid after each experiment except the early ones. One cc. of chromic acid was allowed to trickle through F into E filled with distilled water and became so diluted that it did not attack the grease on the tap C.

The whole apparatus was in a thermostat at 18.0° , the regulation of which was similar to that previously used and described by Brönsted and La Mer.²⁶ The reading of the thermometer in the bath did not vary over several days more than 0.005° ; the temperature of the solution in the dilatometer would certainly fluctuate less than this owing to the insulating property of the glass wall of the dilatometer. The volume of the dilatometer was 165 cc. and the cross-sectional area of the capillary 0.60 sq. mm. The coefficient of expansion of water at 18° is 0.0002 cc. per $^\circ\text{C}$. The observed fluctuations of the height of the meniscus were generally less than 0.1 mm. This corresponds to a temperature fluctuation of $(0.1 \times 0.60)/(165 \times 1000 \times 0.0002) = 0.002^\circ$, that is, a little less than half the fluctuation of the bath itself. Åkerlöf²⁵ gives a similar calculation for his dilatometer, whose dimensions were not very different from those of ours, and finds that a fluctuation of 0.1 mm. corresponds to a temperature variation of only 0.00003° , but he takes the coefficient of expansion of his aqueous salt solutions to be 0.006 per $^\circ\text{C}$., which must be a mistake. If he observed fluctuations in height of the order of magnitude to be expected from his calculation of temperature effect, they must have been due to some other cause; they would not, however, affect the accuracy of his results, as the volume change of the reaction is so great. In our experiments the volume change calculated according to Riiber's²³ data was about 22 cc. mm., corresponding to a rise of 37 mm., of which about 4 mm. would correspond to the change already taken place in the seven minutes required to fill the dilatometer. The readings in the first ten minutes almost invariably seemed to be too low; this is believed to be due to a trace of water trickling down the wall of the capillary.

²⁴ Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

²⁵ Åkerlöf, *This Journal*, **48**, 3046 (1926).

²⁶ Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

The method used for computing the velocity constant was that described by Guggenheim,²⁷ which avoids the unnecessarily large error of the usual formula owing to the great weight given to the end value, whose accuracy is often less than that of the other individual readings. A series of readings V is made at times t spread over an interval two or three times the length of the period of half-completion of the reaction. A second series of readings V' is then made, each at a time $t + \tau$ exactly a constant interval τ after the corresponding reading V , the interval τ being at least two to three times the period of half-completion. If $\log_{10} (V' - V)$ is then plotted against t , a straight line is obtained whose slope is $-k$. The half-time periods of our reactions were generally 30 to 50 minutes, and the period chosen for t was usually 120 minutes. This

TABLE IIA
TYPICAL EXPERIMENT

Experiment 15.21. Sodium *o*-toluate, 0.075 *M*. *o*-Toluic acid, 0.0026 *M*. $k = 6.16 \times 10^{-3} \text{ min.}^{-1}$.

Time, t Min. Sec.		Reading ($\tau = 120 \text{ min.}$) V V'		$V' - V$	\log_{10} ($V' - V$)	$V' - V$ calcd.	Deviation
0	0	4.395	6.50	2.105	0.323	2.105	0.00
2	0	4.475	6.52	2.045	.311	2.04	+ .005
4	0	4.545	6.535	1.99	.299	1.99	.00
6	0	4.615	6.545	1.93	.286	1.93	.00
8	0	4.695	6.565	1.87	.272	1.875	- .005
10	0	4.76	6.575	1.815	.259	1.82	- .005
12	30	4.83	6.59	1.76	.246	1.76	.00
15	0	4.91	6.60	1.69	.228	1.69	.00
18	0	5.00	6.615	1.615	.208	1.625	- .01
21	0	5.09	6.63	1.54	.187	1.555	- .015
24	0	5.17	6.64	1.47	.167	1.49	- .02
28	0	5.27	6.66	1.39	.143	1.41	- .02
32	0	5.37	6.685	1.315	.119	1.33	- .015
36	0	5.45	6.70	1.25	.097	1.26	- .01
40	0	5.53	6.72	1.19	.076	1.19	.00
45	0	5.64	6.735	1.095	.039	1.105	- .01
50	0	5.72	6.76	1.04	.017	1.035	+ .005
55	0	5.805	6.775	0.97	$\bar{1}.987$	0.96	+ .01
60	0	5.89	6.79	.90	$\bar{1}.954$.895	+ .005
65	0	5.96	6.795	.835	$\bar{1}.922$.835	.00
70	0	6.02	6.805	.785	$\bar{1}.895$.775	+ .01
76	0	6.105	6.82	.715	$\bar{1}.854$.715	.00
82	0	6.18	6.835	.655	$\bar{1}.816$.655	.00
88	0	6.235	6.85	.615	$\bar{1}.789$.60	+ .015
95	0	6.31	6.87	.56	$\bar{1}.748$.545	+ .015
102	0	6.38	6.88	.50	$\bar{1}.699$.495	+ .005
110	0	6.44	6.89	.45	$\bar{1}.653$.45	.00
115	0	6.485	6.895	.41	$\bar{1}.613$.41	.00

²⁷ Guggenheim, *Phil. Mag.*, 1, 538 (1926).

TABLE IIB

TYPICAL EXPERIMENT

Experiment 15.11. Sodium *o*-toluate, 0.050 *M*. *o*-Toluic acid, 0.0027 *M*. $k = 5.92 \times 10^{-3} \text{ min.}^{-1}$.

Time, <i>t</i>		Reading ($\tau = 120 \text{ min.}$)		$V' - V$	Log_{10} ($V' - V$)	$V' - V$ calcd.	Deviation
Min.	Sec.	V	V'				
4	0	4.66	6.585	1.925	0.2845	1.915	+0.01
8	0	4.79	6.60	1.81	.258	1.81	.00
11	0	4.88	6.62	1.74	.241	1.74	.00
14	0	4.97	6.645	1.675	.224	1.675	.00
17	0	5.055	6.655	1.60	.204	1.60	.00
20	0	5.135	6.68	1.545	.189	1.54	+ .005
24	0	5.235	6.695	1.46	.164	1.46	.00
28	0	5.33	6.70	1.37	.137	1.375	- .005
32	0	5.425	6.725	1.30	.114	1.305	- .005
36	0	5.50	6.74	1.24	.093	1.24	.00
40	15	5.595	6.765	1.17	.068	1.17	.00
44	0	5.675	6.78	1.105	.043	1.11	- .005
48	30	5.75	6.79	1.04	.017	1.04	.00
53	30	5.84	6.81	0.97	$\bar{1}.987$	0.975	- .005
59	0	5.92	6.825	.905	$\bar{1}.957$.905	.00
65	0	6.005	6.84	.835	$\bar{1}.922$.835	.00
71	0	6.09	6.86	.77	$\bar{1}.887$.765	+ .005
78	0	6.185	6.88	.695	$\bar{1}.842$.695	.00
85	0	6.26	6.89	.63	$\bar{1}.799$.635	- .005
93	0	6.33	6.91	.58	$\bar{1}.763$.57	+ .01
102	0	6.415	6.92	.505	$\bar{1}.703$.505	.00

method of computation was checked in a few experiments by using two different values for τ , and the results of the two computations always agreed to within 0.5% with each other and with that obtained by the usual formula, if one assumed a suitable value for the final reading agreeing within the experimental error of 0.1 mm. with both the observed end value and with the end-value obtained by extrapolation. An example of this test is given in the original paper describing the method.

We give in tabular form the complete data for two experiments. The first column gives the times *t* in minutes and seconds; the second column gives the readings *V* at the times *t*; the third gives the readings *V'* at times *t* + τ where τ is 120 minutes; the fourth gives the values of $\log_{10} (V' - V)$; when these are plotted against *t* the best straight line passes through points corresponding to the values of (*V'* - *V*) given in the sixth column. The last column gives the differences between the figures in the fourth and sixth columns; these differences measure the accuracy of the individual readings. In the first example the deviations were unusually great, whereas in the second experiment they were somewhat less than average.

The glucose used was Merck's best anhydrous α -glucose. Two different preparations were made, and a few experiments performed in duplicate

with the two samples gave identical results. Rough tests with indicators showed the distilled water used, which was presumably saturated with carbon dioxide from the air, to have a P_H between 5 and 6 and this was not appreciably altered by dissolving the glucose. Any trace of acid or alkali in the glucose would be negligible, as almost all the experiments, except those to determine the effect of hydrogen ion, were performed in buffer solutions with a P_H between 4 and 6, the range in which the effects of both hydrogen ion and hydroxyl ion are quite negligible; whenever the buffer solution contained a quantity of weak acid small compared with that of the corresponding salt, the amount of weak acid was checked by titration against very dilute sodium hydroxide, using phenolphthalein as indicator. For the same reason a trace of acid or alkali in the various preparations of weak acids and salts used would be negligible. Whenever there was any possible doubt about the P_H of the solution being within the range 4 to 6 it was tested colorimetrically.

It has been emphasized by Lowry²⁸ that one can never be certain that there is not present some minute trace of an unknown catalyst. But, whatever precautions one took to purify one's material, one could never be sure that this hypothetical catalyst was removed, as long as its nature or even existence was quite unknown. We were therefore satisfied with assuring ourselves that none of the materials used contained as impurity an appreciable quantity of any substance known to be a catalyst. As, however, the velocity constant for a given experiment appeared to be quite definite with an accuracy of 0.5%, as shown by the agreement between two independent computations using different values for the time interval τ , whereas the disagreement between individual experiments was occasionally over 2%, it is just possible that there was sometimes present a trace of such an obscure catalyst whose amount could not be controlled. It is also possible that there may have been some surface reaction at the glass wall varying with the state of the glass; but the regularity of our results indicate that any effects of this type must have been small, not greater than 2%. The only experiments, other than some of the earliest ones, that seem to show irregularities greater than 2% are those in solutions of a strong acid; this may conceivably have been due to some reaction of the acid with the glass. Partly through lack of time, but especially because our main object was to study the effect of catalysts other than hydrogen ion, we did not investigate the cause of the smaller accuracy of the experiments with a strong acid.

For each experiment 200 cc. of solution was made up to a definite concentration in gram molecules per liter. Of this, 180 cc. was used for the experiment, together with 18 g. of glucose; the remaining 20 cc. of solution was used for checking its P_H .

²⁸ Lowry, *J. Chem. Soc.*, 127, 1371 (1925).

6. The "Spontaneous" Reaction and the Hydrogen-Ion Catalysis

Table III gives the results of experiments to determine k_0 , in which experiments the solutions contained, apart from water, no acid or base. The table shows that the value $(5.30 \pm 0.10) \times 10^{-3} \text{ min.}^{-1}$ obtained for k was reproducible at various times over a period of one and a half years, was the same for both preparations of α -glucose and was unaffected by salts up to an ionic strength of 0.2, even with salts containing bivalent and trivalent ions. We therefore consider ourselves justified in refusing to admit the possibility of a neutral salt effect greater than 2% in the dilute solutions used in all our experiments.

TABLE III

EXPERIMENTS TO DETERMINE k_0 AND SHOW ABSENCE OF NEUTRAL SALT EFFECT ($t = 18^\circ$)

Date	Glucose prepn.	Concn. of acid	Concn. neut. salt, moles per liter	$k \times 10^3$ min.^{-1}
19-12-25	I	HClO_4 1.0×10^{-4}		5.20
13-1-26	I	HCl 1.0×10^{-5}		5.23
14-1-26	I	HCl 1.0×10^{-4}		5.31
19-1-26	I	HClO_4 1.0×10^{-4}	NaCl .100	5.25
20-1-26	I	HClO_4 1.0×10^{-4}	KNO_3 .200	5.18
13-9-26	I	HCl 1.0×10^{-4}		5.29
29-9-26	I	HClO_4 1.0×10^{-4}	NaCl .200	5.24
12-10-26	I	HClO_4 1.0×10^{-4}	KNO_3 .100	5.36
14-10-26	I	HClO_4 1.0×10^{-4}	KNO_3 .100	5.40
15-10-26	I	HClO_4 1.0×10^{-4}	KNO_3 .200	5.28
20-10-26	II	HClO_4 1.0×10^{-4}		5.27
21-10-26	II	HClO_4 1.0×10^{-4}		5.27
26-10-26	I	HClO_4 1.0×10^{-4}	$\text{Ba}(\text{NO}_3)_2$.05	5.43
27-10-26	I	HClO_4 1.0×10^{-4}	$\text{Ba}(\text{NO}_3)_2$.025	5.30
6-4-27	II	HClO_4 1.0×10^{-4}	$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$.040	5.36
6-7-27	II	Distilled water ^a		5.42

^a If the water were saturated with carbon dioxide from the air the effect of hydroxyl ion would almost certainly be negligible. As, however, most of the carbon dioxide is probably sucked out before the solution is brought into the dilatometer, the P_{H} of the solution may have been just over 6; this would be sufficient to account for the slightly high value of the reaction rate constant in the experiment with distilled water as solvent.

Table IV gives the results of experiments with perchloric acid solutions to determine the effect of oxonium ion. The results are also shown plotted in Fig. 2, from which the value 0.145 was obtained for $k_{\text{OH}_3^+}$. The last column of the table gives values of $k \times 10^3$ calculated from the formula

$$k = 0.00530 + 0.145 c_{\text{OH}_3^+}$$

where $c_{\text{OH}_3^+}$ is the concentration of hydrogen ion reckoned as equal to the stoichiometric concentration of perchloric acid. As mentioned above this set of experiments is less concordant than any other set, the error of individual experiments being in some cases 3 or 4%. The results are,

TABLE IV
EXPERIMENTS TO DETERMINE THE EFFECT OF OXONIUM ION (t 18°)

Date	Glucose prepn.	Concn. of HClO_4 $\times 10^2$	Concn. neut. salt, moles per liter	$k \times 10^3$, obs.	$k \times 10^3$, calcd.
15-1-26	I	0.10		5.42	5.44
16-1-26	I	0.99		6.67	6.73
18-1-26	I	2.00		8.00	8.20
19-1-26	I	3.00		9.37	9.65
21-1-26	I	4.00		11.26	11.10
25-1-26	I	3.25	$\text{KNO}_3.20$	10.02	10.01
26-1-26	I	1.00	$\text{KNO}_3.20$	6.51	6.75
22-9-26	I	0.96		6.87	6.67
23-9-26	I	1.92		8.28	8.04
25-9-26	I	2.89		9.50	9.41
26-9-26	I	3.85		10.80	10.88
28-9-26	I	4.33		11.38	11.59
11-10-26	I	0.48		6.02	6.00
16-10-26	II	0.48		6.00	6.00
25-10-26	II	2.47		8.92	8.88
8-6-27	II	2.50	$\text{NaCl}.20$	8.89	8.92
9-6-27	II	2.00	$\text{Ba}(\text{NO}_3)_2.050$	8.21	8.20

however, sufficient to show that the effect of oxonium ion is proportional to its concentration and that primary salt effect is undetectable.

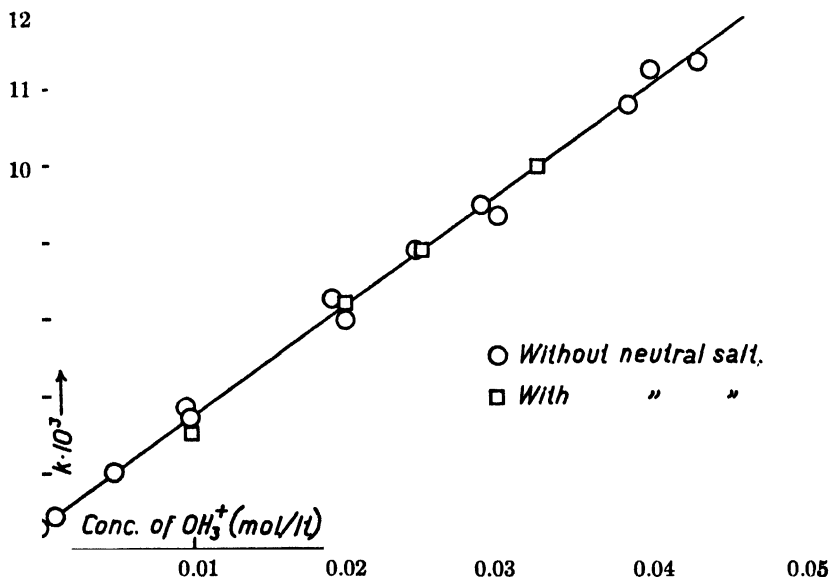


Fig. 2.—Catalysis by hydrogen ions.

Kuhn and Jacob³ claim to have shown that the effect of strong acid is proportional not to the hydrogen-ion concentration but to the hydrogen-

ion activity; but their experiments are not sufficiently accurate to distinguish between activity and concentration in the absence of neutral salt, while those in molar solutions of neutral salt are simply explained by a linear salt effect of the order 10% for a molar solution, which is no more than is to be expected.

TABLE V
EXPERIMENTS TO DETERMINE THE EFFECT OF BASIC ANIONS ($t = 18^\circ$)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
Acetate			
0.020	0.020	5.90	5.88
.025	.025	6.02	6.02
.025	.050	6.00	*6.08
.030	.070	6.37	*6.26
.040	.060	6.63	*6.50
.050	.050	6.83	6.75
.065	.085	7.33	*7.23
.065	.060	7.43	*7.17
.075	.075	7.38	7.47
.090	.110	7.96	*7.95
.100	.100	8.24	8.19
.100	.100	8.22	8.19
.110	.090	8.57	*8.43
.125	.125	8.83	*8.79
.125	.124	8.91	8.91
.200	.198	10.96	11.08
Propionate			
0.010	0.010	5.65	5.60
.030	.070	6.27	*6.29
.040	.020	6.58	6.47
.040	.020	6.53	6.47
.040	.060	6.60	*6.55
.050	.050	6.81	*6.81
.060	.065	7.13	*7.12
.075	.075	7.57	*7.57
.100	.100	7.97	*8.32
.100	.100	8.21	8.32
.110	.115	8.60	*8.63
.125	.125	9.15	9.08
.150	.150	9.85	9.83
Benzoate			
0.040	0.010	5.98	*5.91
.070	.010	6.46	*6.36
.075	.010	6.53	6.44
.090	.020	6.56	*6.67
.100	.020	6.72	6.82
.110	.020	6.83	*6.97
.125	.020	7.12	7.20
.150	.020	7.58	7.58

TABLE V (Continued)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
Formate			
0.040	0.005	6.00	*5.99
.050	.003	6.19	*6.14
.060	.005	6.23	*6.31
.060	.019	6.44	*6.40
.075	.004	6.53	*6.56
.100	.005	6.92	*6.97
.100	.005	7.12	6.97
.125	.006	7.25	*7.39
.125	.005	7.48	7.39
.150	.007	7.78	7.80
.200	.009	8.48	8.44
.250	.014	9.43	9.49
Salicylate			
0.050	0.001	5.45	5.53
.050	.001	5.50	5.53
.075	.001	5.68	5.65
.100	.001	5.77	5.76
Glycolate			
0.050	0.005	6.01	5.96
.075	.005	6.41	6.36
.100	.010	6.75	6.73
.125	.010	7.09	7.07
Chloro-acetate			
0.050	0.0007	5.51	5.57
.075	.0007	5.66	5.70
.100	.001	5.88	5.84
Trimethylacetate			
0.011	0.010	5.63	5.64
.0255	.0245	6.20	6.11
.030	.030	6.21	6.24
.051	.049	6.84	6.91
.0765	.0735	7.66	7.70
Phenylacetate			
0.025	0.006	5.82	5.82
.050	.011	6.44	6.33
.075	.009	6.90	6.83
.100	.009	7.32	7.33
.150	.030	8.41	8.38
o-Toluate			
0.050	0.003	5.92	5.91
.075	.003	6.16	6.21
.100	.005	6.50	6.52
.125	.006	6.84	6.83

TABLE V (Concluded)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
Mandelate			
0.050	0.001	5.80	5.84
.100	.001	6.38	6.38
.125	.001	6.66	6.65
Cyanacetate			
0.100	0.001	5.66	5.68
.125	.001	5.78	5.78
<i>o</i> -Chlorobenzoate			
0.050	0.001	5.60	5.62
.075	.001	5.74	5.78
.100	.001	5.94	5.94

* The experiments marked * were carried out at a considerably earlier period than the similar ones not so marked and in some cases are rather below average accuracy, especially when the reaction rate is high.

7. The Effect of Monobasic Acids and their Anions

In Table V the first three columns give the results of experiments performed to determine the catalytic effect of the anions of weak monobasic acids. All the solutions were made up in such a way that the *P_H* was between 4 and 6; there could therefore be no appreciable catalysis by

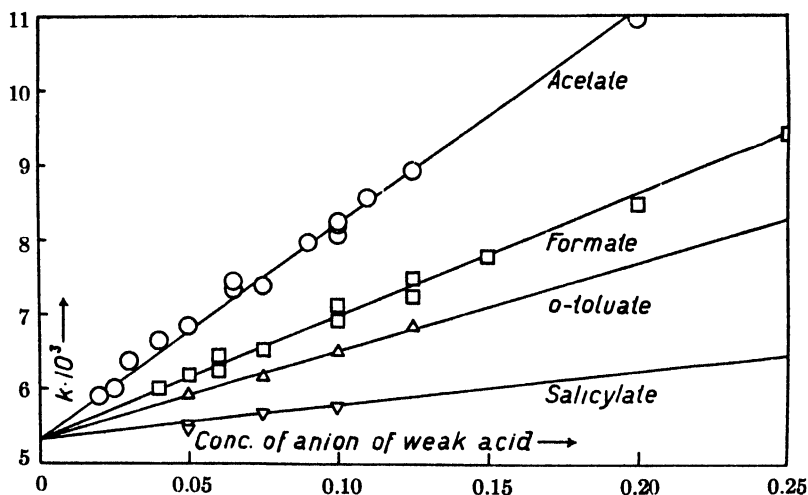


Fig. 3A.—Catalysis by anions.

either hydrogen or hydroxyl ion. As we have already shown that neutral salt effect is certainly not more than 2%, it follows that any considerable increase in the velocity constant can only be due either to the anions, acting as bases, or to the undissociated molecules of the acid. In Figs. 3A, 3B and 3C the values of *k* are plotted against the concentration of

the anion. They leave no doubt that the anions are catalytically active in proportion to their concentration. In the case of the strongest bases trimethylacetate, propionate and acetate ions the effect is over one-fifth

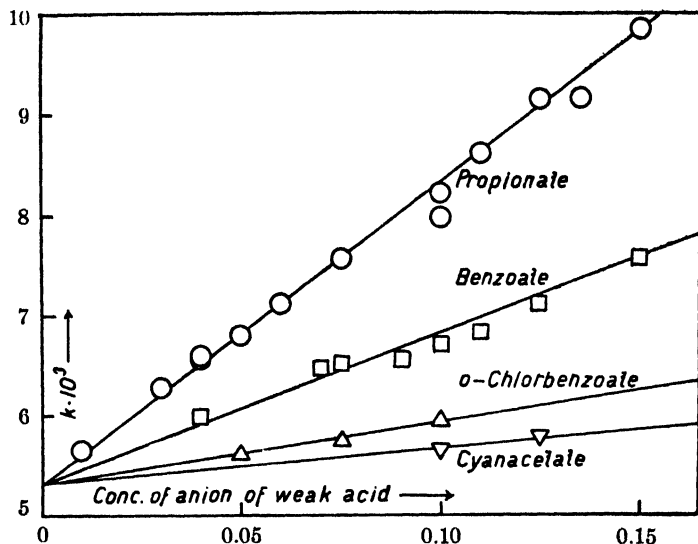


Fig. 3B.—Catalysis by anions.

that of oxonium ion; even cyanacetate ion, the weakest base of this type studied, has an effect about one-fortieth that of oxonium.

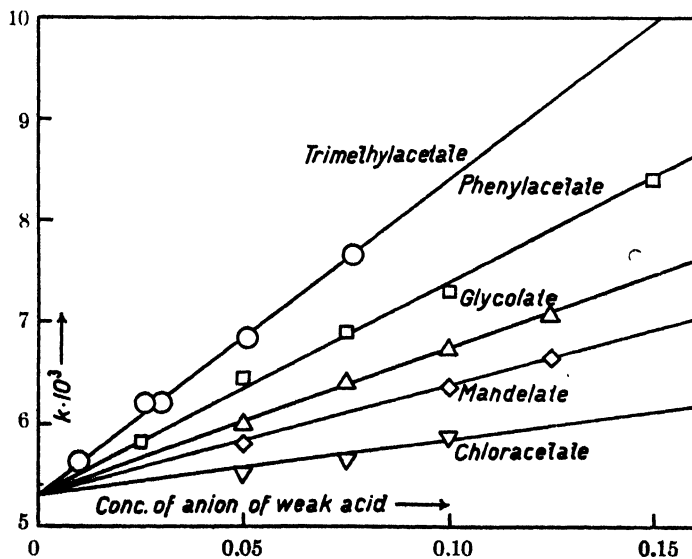


Fig. 3C.—Catalysis by anions.

In the first four columns of Table (VI) are given the results of experiments to determine the effect, if any, of the undissociated acid molecules. The method was to make a series of experiments with a constant concentration of the sodium salt, that is, of anion, and various concentrations of the acid, so far as possible keeping the *P_H* above 4; this was not always possible and in a number of cases the effect of oxonium is not quite negligible; the concentration of hydrogen ion can, however, be calculated approximately from the composition of the buffer solution, using rough values

TABLE VI
EXPERIMENTS TO DETERMINE THE EFFECT OF UNDISSOCIATED ACID MOLECULES
(*t* = 18°)

Concn., sodium salt	Concn., acid	Concn., hydrogen ion × 10 ⁴	<i>k</i> × 10 ³ obs	<i>k</i> × 10 ³ calcd.
Formic Acid				
0.100	0.005	0.1	6.92	6.97
.100	.025	1	7.06	7.06
.100	.050	1	7.24	7.18
.100	.100	3	7.38	7.41
.100	.150	4	7.63	7.64
.125	.005	0.1	7.48	7.39
.125	.006	.1	7.25	7.39
.125	.124	3	7.86	7.93
.125	.250	6	8.50	8.52
Glycolic Acid				
0.100	0.010	0.2	6.75	6.73
.100	.025	1	6.81	6.81
.100	.075	2	7.04	7.09
.100	.100	2	7.26	7.23
Mandelic Acid				
0.100	0.001	0.1	6.38	6.38
.100	.025	2	6.58	6.55
.100	.050	4	6.70	6.71
.100	.100	7	7.04	7.05
Acetic Acid				
0.020	0.020	0.3	5.90	5.88
.020	.105	2	6.10	6.13
.020	.199	3	6.32	6.36
Trimethylacetic Acid				
0.010	0.010	0.2	5.65	5.64
.010	.100	2	5.88	5.84
.0255	.0245	0.2	6.20	6.11
.0255	.100	1	6.26	6.31
.0255	.100	1	6.31	6.31
Phenylacetic Acid				
0.025	0.006	0.2	5.82	5.82
.025	.074	2	5.98	6.03

TABLE VI (Concluded)

Concn., sodium salt	Concn., acid	Concn., hydrogen ion $\times 10^4$	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
Propionic Acid				
0.040	0.020	0.1	6.53	6.47
.040	.020	.1	6.58	6.47
.040	.060	.2	6.60	6.55
.040	.110	.6	6.76	6.66
.040	.160	1	6.77	6.82
Chloro-acetic Acid				
0.100	0.001	0.2	5.88	5.84
.100	.025	6	6.09	6.10
.100	.050	12	6.35	6.35
.100	.075	18	6.62	6.61

for activity coefficients, and the values computed are given in the third column. As we have found k_{OH^+} to be 0.145, a hydrogen-ion concentration of 7×10^{-4} gives a catalytic effect of only $0.10 \times 10^{-3} \text{ min.}^{-1}$ so that the correction to be applied for the oxonium catalysis is never more than 2% except in the experiments with chloro-acetic acid.

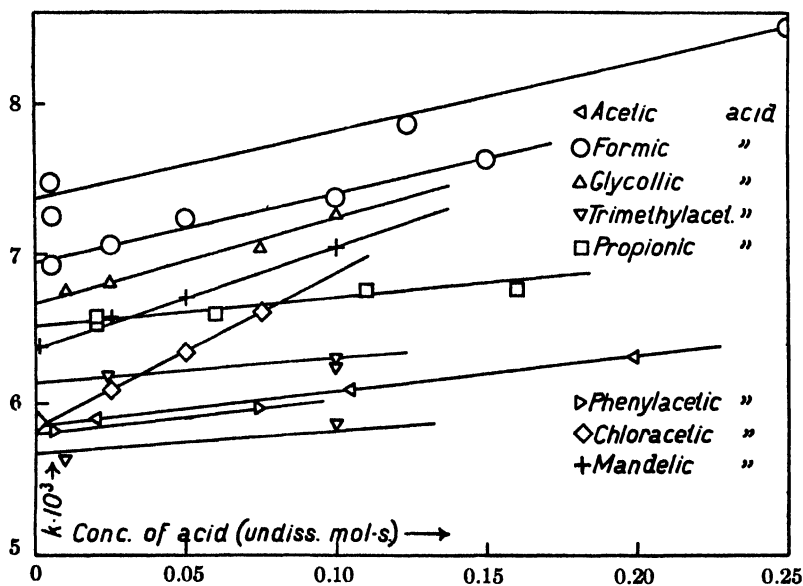


Fig. 4.—Catalysis by anions and undissociated acids.

In Fig. 4 the values of k for each series of constant concentration of sodium salt are plotted against the concentration of acid. The slopes of the straight lines obtained give the values of k_A , the catalytic constants of the various acid molecules, except for the above-mentioned correction

for OH_3^+ catalysis. When two sets of experiments have been made with the same acid, the constant concentration of salt in each set being different in the two cases, two parallel straight lines are obtained; the different intercepts on the k axis correspond to the different concentrations of the catalytic anion. Each straight line as drawn has been made to pass through a point corresponding to a point on the lines in Figs. 3A, 3B, 3C; in other words, the computations of the acid and basic catalytic constants are not independent of each other. The catalytic effect of the undissociated acid molecule seems to be so small in the case of the weakest acids that the existence of any effect might be disputed, but the effect of the formic acid, glycolic acid and mandelic acid molecules is unquestionable. In the case of chloro-acetic acid the hydrogen-ion catalysis, though important, cannot account for more than one-third of the increase in the velocity constant with increasing concentration of acid. With a still stronger acid, such as cyanacetic acid, unless one used a high concentration of the salt, the hydrogen-ion catalysis would always be greater than that of the acid molecules. There is thus in this reaction a real difficulty in detecting this catalysis by undissociated acid molecules; if the acid is too weak the effect is too small to observe; if the acid is too strong the effect is masked by that of oxonium ion and most common acids of suitable strength are insufficiently soluble. The same difficulty may have obscured such an acid catalysis in other reactions where the whole effect has been ascribed to OH_3^+ . Our main evidence for catalysis by the "undissociated" acid molecules must rest on the experiments with formic acid, glycolic acid and mandelic acid; the results obtained with the weaker acids and with chloro-acetic acid, though not convincing by themselves, lend additional support.

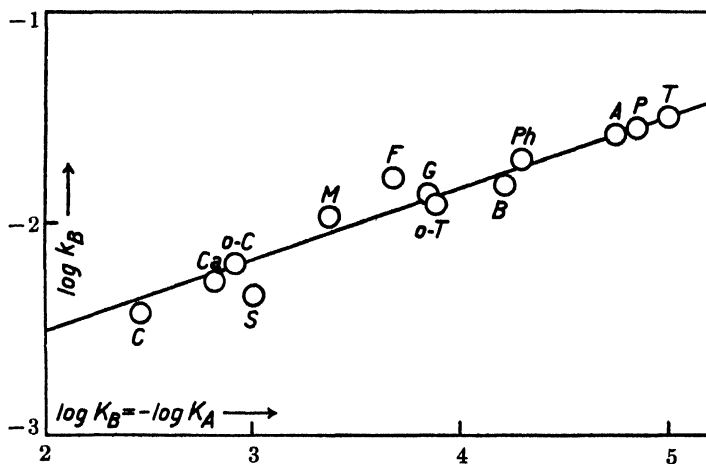
TABLE VII
CATALYTIC CONSTANTS OF UNIVALENT NEGATIVE BASES AND UNCHARGED ACIDS
($t = 18^\circ$)

Acid	Acid (dissoc.) const. $K_A \times 10^4$	Acid catalytic const. $k_A \times 10^8$	Basic catalytic const. $k_B \times 10^8$	$k_B \times 10^8$ theoret.
Trimethylacetic.....	0.10	2.0	31.4	31.5
Propionic.....	.14	2.1	28.1	28
Acetic.....	.18	2.4	26.5	26.5
Phenylacetic.....	.5	2.8	20.0	18
Benzoic.....	.6	...	15.2	17
<i>o</i> -Toluic.....	1.3	...	12.2	13
Glycolic.....	1.4	5.6	13.7	13
Formic.....	2.1	4.6	16.5	11
Mandelic.....	4.3	5.7	10.8	8
Salicylic.....	10	...	4.6	6.5
<i>o</i> -Chlorobenzoic.....	13	...	6.4	6.5
Chloro-acetic.....	15	6.8	5.4	5.5
Cyanacetic.....	35	...	3.8	4

The important question of how the acid and basic catalysis depends upon the strength of the acid or base is answered by the figures in Table VII. Here are given the catalytic constants k_A and k_B calculated from the data of Tables V and VI; the figures in the last column will be explained later. The acids are arranged in order of increasing acid (dissociation) constant K_A . The third column gives k_A the constant for acid catalysis by the "undissociated" molecules and the fourth gives k_B , the constant for the basic catalysis by the anions. The last columns of Tables V and VI give values for k calculated from the formula

$$k = 0.00530 + 0.145 c_{\text{OH}^+} + k_B c_B + k_A c_A$$

where k_B and k_A have the values given in Table VII, c_B and c_A are the concentration of anion (base) and undissociated molecule (acid), respectively.



T, trimethylacetate; Ph, phenylacetate; G, glycolate; S, salicylate; C, cyanacetate, P, propionate; B, benzoate; F, formate; o-C, o-chlorobenzoate; A, acetate; o-T, o-toluate; M, mandelate; Ca, chloro-acetate

Fig. 5.—Dependence of basic catalysis on the strength of the basic anion.

In the experiments of Table V the second term is always quite negligible and the last either negligible or small so that the formula becomes approximately

$$k = 0.00530 + k_B c_B$$

In the data of Table VI the second term is never greater than 0.00010 except in the experiments with chloro-acetic acid and the third term is constant for each series.

Brönsted and Pedersen⁴⁸ found a very simple relation between k_B , the catalytic constant of an anion in the decomposition of nitramide, and K_B , the basic constant of the anion, which by definition is the reciprocal of K_A , the dissociation constant of the conjugate acid. The relation was

$$k_B = 6.2 \times 10^{-5} K_B^{0.88}$$

so that plotting $\log k_B$ against $\log K_B$ they obtained a straight line of slope 0.83. In Fig. 5 we have plotted the results for the anion basic catalysis of the mutarotation of glucose in a similar way. In this case we also obtain an approximate straight line, but the slope is 0.34 and the relation between k_B and K_B is less exact than for the nitramide catalysis. The last column of Table VII gives values of k_B corresponding to the straight line in Fig. 5. These values agree with the observed values in most cases within $2 \times 10^{-3} \text{ min.}^{-1}$, but formate ion is a noticeable exception.

The figures in Table VII show that the acid catalytic constant k_A increases with K_A , as is to be expected, but the range of the accurate values for k_A is so small that it is not worth while attempting to find an empirical relation.

8. The Effect of Other Types of Basic Catalysts

All the basic catalysts so far mentioned have been molecules with one negative charge like hydroxyl ion. Further experiments were performed to show that basic molecules with other electric charges were also effective catalysts. The first uncharged basic molecule tried was aniline, but in this case there was some other reaction as well as the mutarotation; this showed itself by an initial contraction of the solution, the volume reaching a minimum value after about 35 minutes; it was nearly 80 minutes before the volume increase followed the unimolecular law. The disturbing process slowed down more rapidly than a unimolecular process and it therefore seemed probable that there was some combination between the aniline and the glucose, such a reaction being known to take place at high temperatures. Consequently one does not know the concentration of free aniline remaining and so no quantitative conclusions could be drawn from these experiments.

It was thought that with a tertiary base this disturbing reaction should be absent, experiments with pyridine pyridinium perchlorate buffer solutions gave quite normal results showing the pyridine molecule to have a catalytic constant $k_B = 82.2 \times 10^{-3}$ and the pyridinium ion to have no measurable effect. The results are given in Table VIII.

TABLE VIII
EXPERIMENTS WITH PYRIDINE ($t = 18^\circ$)

Concn of C_5H_5N	Concn of $C_5H_5N \text{ HClO}_4$	$k \times 10^3$ min ⁻¹ obs.	$k \times 10^3$ calcd.
0.025	0.025	7.46	7.37
.050	.050	9.29	9.44
.050	.100	9.63	9.44
.050	.200	9.39	9.44
.050	.200	9.47	9.44

Ammonia being a much stronger base than pyridine, it would be expected to be a more powerful catalyst; it is in fact too strong a base for

its effect to be accurately measured, because in ammonia-ammonium buffer solutions the hydroxyl effect will always be great unless the concentration of ammonium salt is great; the difficulty is analogous to that of measuring the effect of the undissociated cyanacetic acid molecules. It will be remembered that when we computed Osaka's data¹⁹ for ammonia-ammonium chloride buffers (see Table I) and assumed hydroxyl ion to be the only catalyst other than water, we found that the solutions with high concentrations of NH_4^+ and NH_3 gave high results for the velocity constants. Now Osaka also performed three experiments in solutions containing ammonium chloride but no ammonia and these show that any possible effect of NH_4^+ up to a concentration of $6-7 \times 10^{-2}$ is undetectable. There remains the possibility of the NH_3 molecules being catalytically active and our experiments with pyridine make this probable. If we assume, as Hudson did in computing Osaka's results, that k_{NH_3} is zero, then the best value for k_{OH^-} is 9120, but if we do not make this unwarranted assumption we find that the data are best fitted by the formula

$$k = 0.0096 + 6200 c_{\text{OH}^-} + 3.2 c_{\text{NH}_3}$$

This is shown in Table IX where k_1 is the value of k obtained from this formula and k_2 from the formula

$$k = 0.0096 + 9120 c_{\text{OH}^-}$$

We do not in any way claim that the values we have assumed for k_{OH^-} and k_{NH_3} are accurate, but only that the k_1 values agree with the data

TABLE IX
OSAKA'S EXPERIMENTS RECOMPUTED ($t = 25^\circ$)

$c_{\text{NH}_4\text{Cl}}$ $\times 10^2$	c_{NH_3} $\times 10^3$	c_{OH^-} $\times 10^3$	$k \times 10^3$ obs.	$k_1 \times 10^3$	$k_2 \times 10^3$
6.67	4.42	1.87	3.60	3.54	2.67
5.00	3.32	1.81	3.35	3.14	2.61
2.25	2.14	2.30	3.26	3.08	3.06
2.25	3.22	3.46	3.82	4.14	4.12
3.33	4.42	3.37	4.46	4.46	4.03
2.25	4.27	4.59	4.94	5.18	5.14
2.25	5.35	5.75	6.40	6.23	6.20
2.25	6.41	6.90	7.05	7.29	7.25

appreciably better than the k_2 values. We shall later give independent evidence that the value chosen for k_{NH_3} is of the order of magnitude to be expected. The ammonia molecule is thus a catalyst about ten times as powerful as hydrogen ion.

While only little is known about the strength of simple basic molecules with unit positive charge, there are a number of acid molecules with three positive charges whose dissociation constants have been determined quite accurately and their conjugate bases with two positive charges are very suitable for our purpose. The catalytic effect of two such ions was measured. The first was $[\text{Co}(\text{NH}_3)_6\text{OH}]^{++}$ of which the conjugate

acid is the well-known roseo ion $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{+++}$. The second was the green ion $[\text{Cr}(\text{OH}_2)\text{OH}]^{++}$ conjugate to the blue acid $[\text{Cr}(\text{OH}_2)_6]^{+++}$. The results of these experiments are given in Table X. The last column

TABLE X
EXPERIMENTS TO DETERMINE THE EFFECT OF BASIC CATIONS ($t = 18^\circ$)

Concn. of salt with basic cation	Concn. of salt with acid cation	Concn. of salt with neutral cation	$k \times 10^4$ obs.	$k \times 10^4$ calcd.
$[\text{Co}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$ 0.0002	$[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ 0.020	NaClO_4 0.0002	5.49	5.46
$[\text{Co}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$.0020	$[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$.020	NaClO_4 .0020	6.82	6.86
$[\text{Co}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$.0020	$[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$.040	NaClO_4 .0020	6.82	6.86
$[\text{Co}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$.0010	$[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$.020	NaClO_4 .0010	6.13	6.08
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0011	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0009	NaCl .0010	5.83	5.76
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0021	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0019	NaCl .0020	6.38	6.18
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0031	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0029	NaCl .0030	6.66	6.63
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0041	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0019	NaCl .0040	6.87	6.98
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0041	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0039	NaCl .0040	6.85	6.98
$[\text{Cr}(\text{OH}_2)_5\text{OH}]\text{Cl}_2$.0051	$[\text{Cr}(\text{OH}_2)_5]\text{Cl}_3$.0049	NaCl .0050	7.31	7.38
	$[\text{Co}(\text{NH}_3)_5](\text{NO}_3)_3$ 0.040		5.36	5.30

gives values calculated for k assuming that the acid ions are catalytically inactive while the basic ion $[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$ has a catalytic constant $k_B = 0.78$ (five times that of oxonium) and the basic ion $[\text{Cr}(\text{OH}_2)_5\text{OH}]^{++}$ has a catalytic constant²⁹ $k_B = 0.41$.

The last experiment in the table shows that the luteo ion $[\text{Co}(\text{NH}_3)_6]^{+++}$, whose structure is extremely similar to that of the roseo ion $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{+++}$ but which unlike the roseo ion is neutral, has no detectable effect. It appears that primary salt effect is negligible even with trivalent ions at the concentrations of these experiments.

The catalytic effect of bases with two positive charges is considerably greater than that of a base of the same strength with a negative charge. This agrees with the results obtained in the nitramide reaction, which is extremely sensitive to the influence of such ions.

Finally, as an example of a base with two negative charges, the sulfate ion was chosen. Whereas the acid constant of sulfuric acid is immeasurably great, that of the bisulfate ion³⁰ is 1.15×10^{-2} . Hence the sulfate ion SO_4^{--} is a somewhat weaker base than cyanacetate and would thus be expected to have only a small effect. Provided, however, this effect is not too small to be detected at all, it will be simpler to measure than that of, say, oxalate ion; for in order to suppress the hydroxyl-ion concentration in oxalate solutions one would have to have present, as well as $\text{C}_2\text{O}_4^{--}$, a quite considerable amount of HCO_4^- ; but HCO_4^- is both an acid and a base and so its catalytic properties might not be simple. With sulfate solutions, however, the merest trace of excess acid is sufficient to keep the P_H well below 6. The solutions used were made up as follows. To a volume of standard sulfuric acid enough standard sodium hydroxide

²⁹ A possible effect of the $[\text{Cr}(\text{OH}_2)_4(\text{OH})_2]^+$ -ion has been disregarded in this calculation.

³⁰ Sherrill and Noyes, *THIS JOURNAL*, **48**, 1861 (1926).

was added to make the solution just alkaline to methyl red; two or three drops of normal acetic acid were then added to bring the solution to the acid side of the methyl red end-point; the solution was then diluted to the required extent. The value found for $k_{\text{SO}_4^{--}}$ was 4.0×10^{-3} . The results are given in Table XI

TABLE XI
EFFECT OF SULFATE ION ($t = 18^\circ$)

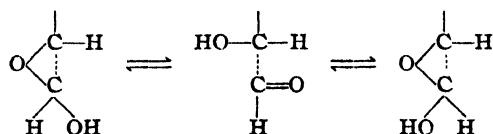
Concn. Na_2SO_4 , moles per liter	Concn. of acetic acid	$k \times 10^3$ min^{-1} obs.	$k \times 10^3$ calcd.
0.050	10^{-4}	5.55	5.50
.075	10^{-4}	5.60	5.60
.100	10^{-4}	5.67	5.70

9. Interpretation of the Spontaneous Reaction and the Mechanism of Mutarotation

We have now obtained evidence that in dilute aqueous solution any molecule, charged or neutral, if a sufficiently strong base or acid, will increase the velocity of mutarotation in proportion to the concentration at which it is present. There remains the question of interpreting k_0 the minimum value of k , or constant of the "spontaneous" reaction in aqueous solution. It was suggested in the work of Brönsted and Pedersen^{4a} that the "spontaneous" nitramide decomposition is actually a basic catalysis by the solvent molecules, and a similar interpretation in the case of the mutarotation seems very plausible. Much light is thrown on this question by the work of Lowry and others³¹ on tetramethylglucose. This sugar has approximately the same rate of mutarotation in water as glucose and has the advantage of greater solubility in anhydrous solvents and can be obtained in a much purer state. Lowry and Richards have succeeded in showing that in dry ethyl acetate the mutarotation of tetramethylglucose could be arrested over a period of about 24 hours; in chloroform containing a trace of phosgene, which removes organic bases, an arrest was obtained over a period of 10 days. We do not wish to enter into a discussion of whether mutarotation takes place not at all or only extremely slowly in a pure inert solvent, but it is at any rate established that the actually observed minimum rate in water is due practically entirely to the water itself. In other words, the OH_2 molecule is a catalyst to which we can assign a catalytic constant $k_3/55.6 = 9.5 \times 10^{-5}$. (As in assigning values to the acid and basic constants of OH_2 we had to ignore the association of the water, we have to do the same in assigning a value to its catalytic constant; as our purpose is eventually to discuss the interdependence of these constants these errors will to some extent balance each other.) The next question that suggests itself is whether the OH_2 molecule acts

³¹ (a) Lowry and Richards, *J. Chem. Soc.*, 127, 1385 (1925). (b) Lowry and Faulkner, *ibid.*, 127, 2883 (1925); (c) 128, 1938 (1926).

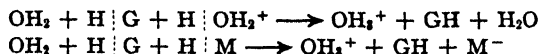
as an acid or as a basic catalyst. This question has also been answered by Lowry^{31b} who showed that the rate of mutarotation of tetramethyl-glucose in dry pyridine, a base, and in dry cresol, an acid, was less than 3% of its rate in water, but that by using as solvent mixtures of pyridine and cresol high rates could be obtained up to twenty times that in water. Lowry²⁸ interprets this to mean that both an acid molecule and a basic molecule take part in the reaction. It is generally agreed among organic chemists that in the change from α -glucose to β -glucose the aldehyde form of glucose is an intermediate product.



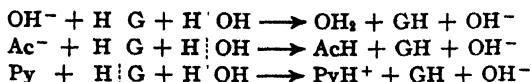
There is a considerable difference of opinion as to which of these three forms may be hydrated, but this question need not concern us. The fact that mutarotation follows the unimolecular law can be simply interpreted only by assuming that the change from the α - or β -form to the aldehyde form is slow compared with the change from the aldehyde form to either of the others. Thus the observable rate of the mutarotation is determined by the velocities of the change from α - or β -form to aldehyde form, processes involving only a change of position of one proton. Lowry's²⁸ interpretation of the mechanism of the catalysis is that the basic catalyst removes a proton from one part of the glucose molecule and the acid catalyst supplies a proton to another part of the molecule. If we write symbolically HG for α -glucose and GH for the aldehyde form, then the mechanism of the primary process in water is, in the absence of other catalysts



where one OH_2 molecule acts as an acid and one as a base. In catalysis by oxonium ion OH_3^+ , or by an undissociated molecule of mandelic acid MH , an OH_2 molecule acts as a base.



In catalysis by hydroxyl ion OH^- , or by acetate ion Ac^- or by the pyridine molecule Py , one molecule of OH_2 acts as an acid.



We have given these processes in some detail because, while entirely agreeing with Lowry as to the reasonableness of this mechanism, we consider that in his own description of it there is some confusion between the catalytic effect of the hydroxyl ion in an aqueous solution of pyridine

and the effect of the pyridine molecule itself; except in solutions containing very little water the former effect will be the greater of the two. We also wish to emphasize the similar catalytic action of the various bases, regardless of their electric charge, and likewise the similar catalytic action of the several types of acids.

10. The Interrelation between Strength and Catalytic Effect of Acids and Bases

The question of an interrelation between the strength and the catalytic activity of acids and bases has already been considered in Section 7 for the case of univalent basic anions. Evidence from the later sections permits of a more general discussion of this problem and also a very considerable extension of the region of acidity and basicity considered.

The data for typical acid and basic catalysts of various types are given in Table XII. The first two columns give a number of conjugate acid-base pairs of various types; the third column gives values of K_A for the

TABLE XII
CATALYTIC CONSTANTS ($t = 18^\circ$)

Acid	Base	K_A	k_A	k_B
OH_3^+	OH_2	5.6×10	1.4×10^{-1}	9.5×10^{-5}
OH_2	OH^-	1.0×10^{-16}	9.5×10^{-5}	$^a 6 \times 10^3$
Mandelic acid	Mandelate ion	4.3×10^{-4}	6×10^{-3}	1.1×10^{-2}
Acetic acid	Acetate ion	1.8×10^{-5}	2×10^{-3}	2.7×10^{-2}
Pyridinium ion	Pyridine	3.5×10^{-6}		8.3×10^{-2}
$[\text{Co}(\text{NH}_3)_6\text{OH}_2]^{+++}$	$[\text{Co}(\text{NH}_3)_6\text{OH}]^{++}$	1.6×10^{-6}		7.8×10^{-1}
Ammonium ion	Ammonia	3.2×10^{-10}		$^a 3.2$
HSO_4^-	SO_4^{--}	1.2×10^{-3}		4×10^{-3}

^a At 25° .

acid; the fourth gives the catalytic constant k_A for the acid and the fifth the catalytic constant k_B for the base. In Fig. 6, $\log k_A$ and $\log k_B$ are plotted against $\log K_A$. Included in the table are the values of k_B for hydroxyl ion and the ammonia molecule computed from Osaka's data; these values are halved in the plot because Osaka's experiments were at 25° whereas our own were at 18° , a correction which is not of great importance.

The plot shows the points corresponding to basic catalysis to lie approximately on a straight line except for the bases having a double positive charge. The slope of this line is 0.42, while for univalent anions, as mentioned, the slope 0.34 was found. The values for OH^- and OH_2 , however, are uncertain for several reasons. For instance, in basic solution, in addition to the OH^- ion, there will exist strongly basic glucose anions which may have a considerable catalytic effect and so make the OH^- ion appear more effective than it actually is. It should be noted also that no attention has been paid here to the influence of statistical factors,^{2,4a} such as would

be necessary for the establishment of an exact relation between the strength and the catalytic effect of an acid or base.

The position of the point for the NH_3 molecule justifies our belief that the value computed from Osaka's data is at least of the right order of magnitude.

The basic molecules with two positive charges seem to possess a particularly strong basic effect. This agrees with the results found in the nitramide catalysis and also with theoretical considerations.²

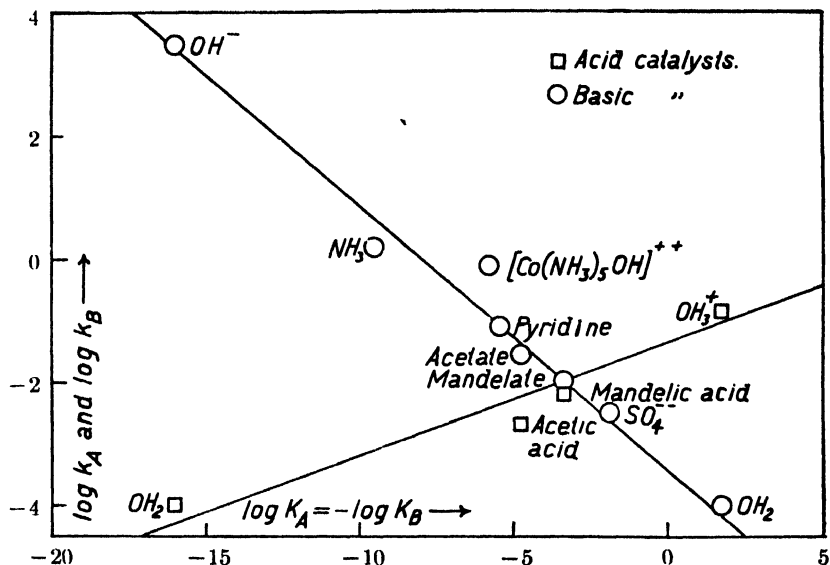


Fig. 6.—Dependence of acid and basic catalysis on the strength of acid and base.

The curve for acid catalysis is not so well established as the one for basic catalysis, but the increasing catalytic effect with increasing acid strength is obvious. When one considers that the plot covers a range of 10^{18} in K_A and of 10^8 in k_B , the connection between the catalytic effect of an acid or base and its strength is striking. It indeed appears that one could predict the catalytic effect, at least correct to one power of 10, of any acid or basic molecule or ion merely from the knowledge of its strength.

Summary

1. In correspondence with an extended conception of acids and bases a new theory of acid and basic catalysis has been presented, in which the catalytic effect is ascribed, not particularly to the hydrogen and hydroxyl ion, but to the action of acid and basic molecules in general. Previous work in the field has been discussed and criticized.

2. The mutarotation reaction of glucose has been studied by a dilato-

metric method under the influence of a number of acids and bases of various electric charge types. The results of the experiments have given strong support to the theory presented.

3. The catalytic effect of acid and basic molecules on the mutarotation of glucose increases with their strength as acids and bases. There seems to be a simple relationship between catalytic efficiency and strength, shown by the fact that a logarithmic plot of the basic catalytic constant against the basic strength constant, covering the range of 10^{18} in the latter, comes out approximately as a straight line with slope about 0.4.

4. The laws of mutarotation are in marked conformity with the laws previously found for the decomposition of nitramide.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

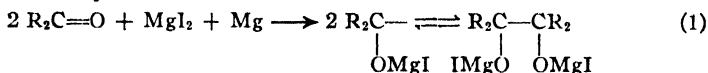
THE REDUCTION OF BENZIL BY THE BINARY SYSTEM, MAGNESIUM + MAGNESIUM IODIDE (OR BROMIDE)

BY M. GOMBERG AND W. E. BACHMANN

RECEIVED JULY 18, 1927

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Recently we described the reducing action of a mixture of magnesium iodide (or bromide) and magnesium on aromatic ketones.¹ This class of ketones was found to give pinacolates through the intermediate formation of free radicals, ketyls

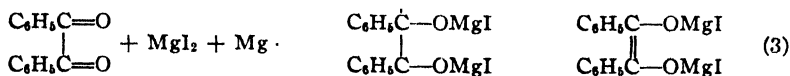


According to our hypothesis, the active reducing agent was magnesium subiodide, generated by the interaction of the metal and halide



and present as such only in minute quantities at any one moment. The reaction has now been extended to the diketone, benzil.

Benzil with its two carbonyl groups reacts with the binary system fundamentally in much the same fashion as do the aromatic ketones, except that here the newly created carbon-carbon bond remains within the original molecule, giving rise, therefore, to an unsaturated glycolate.

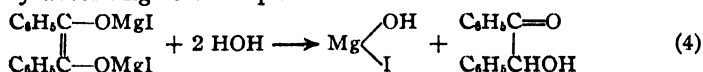


The reaction proceeds *quantitatively* according to the above equation. In the process of reduction the solution displays a series of deep colors, green, brown, red and finally yellow. The halomagnesium glycolate

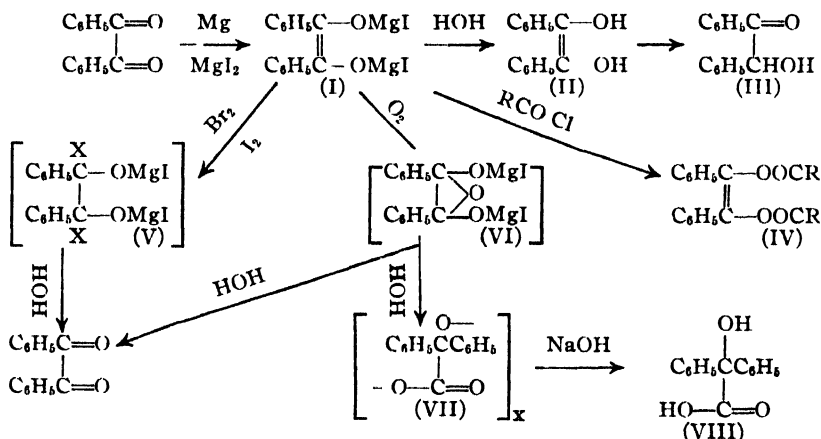
¹ (a) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927); (b) Gomberg, *Chem. Reviews*, **2**, 309 (1925).

(I) was isolated in solid, crystalline state; it was found to be colorless and to have the composition indicated by the formula.

On hydrolysis this glycolate gives the unsaturated glycol, stilbene-diol, $C_6H_5C(OH)=(HO)CC_6H_5$ (II), which tautomerizes rapidly to the stable form, benzoin (III). Titration of the magnesium hydroxide and estimation of the benzoin produced showed that the hydrolysis proceeds quantitatively according to the equation:



Like the benzil dipotassium compound, $(C_6H_5COK=)_2$, of Staudinger and Binkert,² and the benzil disodium derivative of Nef,³ the unsaturated halomagnesium glycolate reacts with benzoyl chloride and gives α,β -dihydroxystilbene dibenzoate (IV); with acetyl chloride the corresponding diacetate is formed.



Benzyl chloride and methyl iodide were used in the attempt to make ethers, but not much reaction took place with these reagents. With triphenylchloromethane, however, a decided reaction occurred with the formation of benzil and triphenylmethyl.

Iodine and bromine are absorbed mole for mole by the halomagnesium glycolate, the resulting mixtures on hydrolysis giving practically quantitative yields of benzil. The reaction is best formulated as giving the hypothetical compound (V), although it is equally probable that the halogen may detach the MgI without previously adding itself to the glycolate. The reaction with bromine requires but a few minutes; that with iodine is slower.

Considerable heat is generated on exposing the solid glycolate to the air. A solution of the compound, which is transparent and light yellow in

² Staudinger and Binkert, *Helv. Chim. Acta*, 5, 703 (1922).

³ Nef, *Ann.*, 308, 287 (1899).

color, instantly becomes opaque, dark brown in color through the action of even a minute amount of oxygen. The total amount of oxygen that can be taken up corresponds to one atom of oxygen for one mole of glycolate. The primary products of oxidation are probably in the form of an oxide (VI). Addition of water yields benzil and a compound that gives benzoic acid on hydrolysis and may be considered as a polymer of the anhydride of this acid (VII); frequently some benzoic acid is also produced. Because of the extreme sensitivity of the glycolates to oxygen, great care had to be exercised throughout this work to prevent undue exposure to air.

Not only the binary system magnesium-magnesium halide can accomplish the reduction of benzil, but other systems as well can bring about the same reaction with varying degrees of rapidity, even when the metal element is not the same as the metal in the halide.

In view of the remarkable reactivity of the glycolate, is it not possible that we have here a partial opening of the double bond to a single bond, giving rise to two reactive trivalent carbon atoms in the same molecule? Similar explanations have been advanced in order to account for the unusual reactivity of certain compounds.⁴

Experimental

Reduction of Benzil.—(a) By $\text{MgI}_2 + \text{Mg}$. A solution of magnesium iodide was prepared from 5.2 g. (0.04 atom) of iodine and excess of powdered magnesium in a mixture of 20 cc. of anhydrous ether and 40 cc. of dry benzene. The colorless solution was filtered into a 70cc. test-tube and 4.20 g. (0.02 mole) of benzil was added; a reddish colored solution resulted at this point, due in part to liberation of iodine (see discussion, p. 2591). A weighed rod of magnesium (8.9900 g.) was inserted and the tube carefully stoppered with a cork. Almost immediately red streamers began to flow from the rod and the solution soon possessed a deep reddish-brown color. After a time the color changed to an opaque greenish-black. In the course of 18 hours the solution became lighter in appearance, shifting to a reddish-brown, then to red and finally to a light yellow color. At the end of the reaction a perfectly clear, transparent solution remained. The rod was removed, and it now weighed 8.5020 g., which represents a loss of 0.4880 g. The theoretical value (Equation 3) is 0.4864 g. (0.02 atom). Dozens of such estimations gave values differing by only a few milligrams from the theoretical.

By using an excess of magnesium turnings complete reduction was effected in one hour; when magnesium powder was employed 10–20 minutes were sufficient to carry 4.20 g. of benzil through the color changes just described. When exactly 0.4864 g. of magnesium turnings was added to 4.20 g. of benzil, the latter was completely reduced and no trace of metal remained at the end of the reaction. The advantage of using a rod is obvious; it can be readily withdrawn from the solution at any time and weighed, thus allowing the reaction to be studied on a strictly quantitative basis.

(b) By $\text{MgBr}_2 + \text{Mg}$. The procedure here was identical with that above except for the preparation of the halide. The synthesis of magnesium bromide from the elements is not feasible; accordingly it was prepared⁵ from mercuric bromide and mag-

⁴ (a) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 247 (1927); (b) Ingold and Marshall, *J. Chem. Soc.*, **129**, 3080 (1926); (c) Zelinsky and Kozeschkow, *Ber.*, **60**, 1108 (1927); (d) Scholl, *Ber.*, **60**, 1236 (1927).

⁵ Ref. 1 a, p. 245.

nesium. Five g. of dry mercuric bromide is placed in a flask with 25 cc. of ether and 10 cc. of benzene, a reflux condenser being provided. One and one-half g. of magnesium powder is now added, followed by 30 cc. of benzene and then the mixture is boiled until reaction is complete. After the mixture has stood for a time the supernatant liquid is decanted through a hardened filter paper; there is thus obtained a pure, colorless solution of anhydrous magnesium bromide. As a rule the mixture was filtered into a narrow graduated cylinder, 1 cc. of the solution removed, decomposed with water, and the concentration of $MgBr_2$ determined by titration with silver nitrate solution. The exact volume of the salt solution requisite for the experiment could now be calculated. The above ether-benzene mixture is capable of dissolving magnesium bromide to the extent of 0.75–0.80 *N*.

For most experiments we used solutions of the glycolate, prepared as above, since the isolation of the solid glycolate itself is accompanied by loss of material. Usually the iodide was used because of the ease of its preparation. For some purposes, as in the study of the color phenomena, the bromide proved more suitable; this was also the case when it was desired to isolate the reaction products in the solid state, the bromide being less soluble than the iodide.

Isolation and Analysis of the Bromomagnesium Glycolate.—This compound is quite soluble when the proportion of benzene to ether is large. In ether alone it is not very soluble, but the reduction of benzil in this solvent is ever so much slower, due to the formation of some magnesium etherate compound in the form of an insoluble oil. Excellent reduction and precipitation occurs in a mixture of solvents consisting of 1 part of benzene to 3 parts of ether. Furthermore, this mixture dissolves magnesium bromide more readily than one richer in benzene.

A solution of magnesium bromide was prepared from 20 g. of mercuric bromide and magnesium in 54 cc. of ether and 18 cc. of benzene. Eight and four-tenths g. of benzil was added and a rod of magnesium inserted. In ten minutes the solution became green, and this color persisted for two days, when the solution became brown. Several days later the reduction was complete; however, shaking was continued for several weeks. During this time a large amount of white, granular glycolate precipitated out. The crystals were filtered from the solution and washed several times with ether-benzene mixture (3:1) and finally with ether alone. After the free solvent had been removed, the crystals weighed 9.82 g. All operations were carried out in an atmosphere of dry nitrogen, for the glycolate is extremely sensitive to oxygen and moisture.

Weighed samples of the solid were decomposed with water; the magnesium hydroxide thus produced was determined by titration with acid; the bromine by titration with silver nitrate; and the benzoin, containing a small amount of oxidation products, was isolated, dried and weighed. On a separate sample the total magnesium was determined as MgO by ignition with nitric acid. The solvent of crystallization was obtained by difference, and it was found that the glycolate crystallized with two molecules of ether. From the results of analysis, the percentages of the constituents were calculated on a solvent-free basis. The results given below were obtained on samples each of which came from a different reduction experiment.

Anal. Subs., 4.982, 1.197, 3.750. Calcd. for $(C_8H_6COMgBr)_2$: benzoin, 50.3; Mg, 11.6; Br, 38.3. Found: benzoin, 49.9, 50.6, 49.1; Mg, 12.6, 11.6, 11.7; Br, 38.3, 37.8, 39.2.

Reduction of Benzil to Glycolate is Quantitative.—Since the glycolate is somewhat soluble it cannot be isolated in quantitative yields from the reduction mixture. We

have proved, however, that the reduction of benzil to the glycolate is, nevertheless, quantitative, by hydrolyzing the reduction mixture itself without previous isolation of the solid glycolate. Repeated runs on 4.20g. samples of benzil gave with water yields of benzoin corresponding to 92–95%. Finally, an experiment was carried out, with rigorous exclusion of air throughout, in which one-tenth of a mole of benzil was reduced, the solution hydrolyzed and the amounts of the components carefully determined.

The colorless solution of magnesium iodide from 28 g. of iodine and 5 g. of magnesium in 50 cc. of ether and 200 cc. of benzene was filtered into a 300cc. Drechsel bottle filled with nitrogen and containing 21.00 g. of benzil. A dark red solution resulted. A weighed rod of magnesium was inserted and the bottle was tightly stoppered by means of a cork. Reaction began immediately with the characteristic production of successive color effects. At the end of 45 hours the solution was light yellow; no precipitate of any kind was present. The magnesium rod was withdrawn, washed, dried and weighed. Loss in weight, 2.435 g.; calculated, 2.431 g.

The clear ether-benzene solution was poured into water which had been freed from air by boiling. Dilute sulfuric acid was used to dissolve the copious precipitate of magnesium hydroxide that had been produced. One and one-half liters of benzene was required to dissolve the benzoin that had crystallized out. The solution was filtered from the small amount of insoluble white substance, which consisted of oxidized glycolate with some magnesium hydroxide adsorbed or occluded. This product weighed 0.25 g., and gave on hydrolysis with sodium hydroxide 0.17 g. of benzilic acid. The main solution was extracted with dilute sodium carbonate and this alkaline solution gave an additional 0.08 g. of benzilic acid.

After the treatment with sodium carbonate, the ether-benzene solution was dried over calcium chloride and the solvent removed by distillation. The white, solid residue, consisting of benzoin and a small amount of benzil, was digested with 70 cc. of cold anhydrous ether in order to remove the benzil, the mixture was filtered, and the undissolved benzoin was washed with ether, in which it is only slightly soluble. The ethereal extract was evaporated to dryness and the light yellow solid was extracted in a Soxhlet extractor with 30–40° petroleum ether. The benzoin is almost completely insoluble in this solvent while the benzil is readily soluble. The separation is as nearly quantitative as can be desired. In the extraction thimble was left 0.32 g. of benzoin; from the petroleum ether extract was obtained 0.42 g. of benzil. In spite of all precautions taken, there still resulted some oxidation of the glycolate to benzil and polymerized benzilic acid. The results may be summarized as follows: benzoin, 20.48 g. (96.6%); benzil, 0.42 g. (2.0%); polymer + benzilic acid, 0.25 g. (1.2%).

We feel justified, therefore, in stating that the reduction of benzil to glycolate is quantitative. In using for our many experiments the reduction solution of benzil without previous isolation of the glycolate, we have thus taken for granted that the amount of glycolate in the solution corresponds exactly to the amount of benzil taken.

The reaction of benzil with magnesium may proceed to completion, although more slowly, in the presence of even small amounts of magnesium halide. For example, yields of benzoin amounting to 78–94% were obtained, though the amount of magnesium halide was only 1–25% of a mole. In all cases the theoretical amount of magnesium was dissolved. As happens with the pinacolates,⁶ the metal halide is continuously split off from the halomagnesium glycolate and is thus made available for

⁶ Ref. 1, p. 243.

further reaction. The magnesium glycolate, $\text{C}_6\text{H}_5\text{C}=\text{CC}_6\text{H}_5$, is less

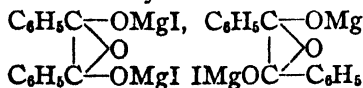
$$\begin{array}{c} \text{OMgO} \end{array}$$

soluble than its precursor and so precipitates out as a colorless solid during the reduction.

Reaction with Oxygen.—The amount of oxygen that can be taken up by the glycolate was measured by means of the absorption apparatus usually employed for similar purposes in the study of free radicals. In the gas buret was placed the same mixture of solvents as was used for the solution of the glycolate, and the bottle was shaken by mechanical means. A solution of the glycolate from 2.10 g. of benzil was connected to the absorption apparatus. Soon the solution became dark brown as the oxygen was taken up. The total volume absorbed was 97 cc. (corr.); calculated for one atom of oxygen to one mole of glycolate, 112 cc. Absorption was rapid at the beginning, gradually becoming slower. Hydrolysis showed the presence of 5% of unoxidized glycolate, 40% of benzil, 40% of benzilic acid polymer and 13% of benzoic acid.

A number of experiments were performed in which the amount of oxygen was not measured, dry air or oxygen being passed through the solution of the glycolate until oxidation was complete. Both the bromomagnesium and the iodomagnesium salts of the stilbene-diol yield the same products on oxidation, benzil (43–73%), benzilic acid, free and as polymer, (17–32%) and benzoic acid (5–16%). The bromomagnesium glycolate becomes colorless on oxidation while the iodomagnesium compound liberates a large amount of iodine. Staudinger and Binkert² obtained only benzilic and benzoic acids and no benzil on oxidation of the potassium salt of the stilbenediol.

Although oxidation of the glycolate and subsequent hydrolysis of the product results in the production of benzil and polymerized benzilic acid, yet very little, if any, of these are present as such in the solution before water is added. Repeated experiments have shown that colorless solutions of completely oxidized bromomagnesium glycolate, when subjected anew to re-reduction with magnesium, display no characteristic color phenomena and no loss of metal occurs. The benzil and the polymer prior to hydrolysis must, therefore, exist in the form of some non-reducible magnesium compound such as the oxide (VI). Whether on oxidation only a single compound (VI) is formed, which on hydrolysis gives rise to the two substances, benzil and polymer, or whether these two substances come from two distinct oxidation products cannot be decided at this time. It is not unlikely that two stereo-isomeric oxides are produced, *cis* and *trans*,



on hydrolysis gives benzil; the other, either before or after hydrolysis, under-

goes rearrangement to the benzoic acid derivative. Other derivatives of the glycol are known to exist in two forms.²

Color Effects during Reduction.—Although the halomagnesium glycolates are colorless in the solid state and are only light yellow in solution, yet when mixed with benzil, especially in equivalent amounts, deep brown solutions are produced. The same colors persist in the solution during reduction of benzil to the glycolate as long as any unreduced benzil is present. They are also formed when the colorless glycolate becomes partially oxidized by air. Under certain conditions the initial color produced on reduction of benzil is brilliant emerald-green. The bromide forms this most readily, solvent and concentration being important factors upon which the formation of the green color depends. Ether was found to favor the formation of green, benzene that of red. With magnesium bromide the initial color is green even with benzene-ether in the ratio 1:1; with magnesium iodide the red color usually appeared, but by using almost entirely ether, green also could be obtained. Moreover, dilution of a green mixture gave a reddish-brown color.

Characteristic color effects have been obtained also in the case of the sodium and potassium derivatives of benzil. Schlenk and Thal⁷ consider the blue compound which they obtained to be a substance containing

a trivalent carbon atom, $C_6H_5\overset{\diagup}{C}(OK)-COC_6H_5$; Nef and Staudinger and Binkert are of the opinion that this compound is the quinhydrone, $[C_6H_5\overset{\diagup}{C}(OK)=(KO)CC_6H_5][C_6H_5\overset{\diagdown}{C}O-COC_6H_5]$. Whether in our case

the green color represents a free radical, $RC(OMgX)-COR$, or whether both the green and the brown are two distinct quinhydrone compounds, each requiring certain specific conditions for existence, is left undecided.

Reaction with Benzoyl Chloride and with Acetyl Chloride.—The clear yellow solution of the glycolate prepared from 4.20 g. of benzil was treated with a solution of 6 g. of benzoyl chloride in 15 cc. of ether and 30 cc. of benzene. In three minutes a white precipitate of magnesium salt began to settle out. After the mixture had stood for 15 hours water was added. The crude product obtained from the organic solvents was recrystallized by dissolving it in a small amount of hot benzene and adding petroleum ether. The dibenzoate of the stilbene-diol was obtained in the form of large, glistening crystals, m. p. 157–158°; reported in the literature, 159°; yield, over 75% of that possible. In like manner the corresponding diacetate was prepared; m. p. 116–117°. Nef and Staudinger and Binkert give 118–119°.

Reaction with Alkyl Halides.—A warm solution of triphenylchloromethane in 20 cc. of benzene was added to a solution of iodomagnesium glycolate from 3.00 g. of benzil, care being taken to prevent access of air. As the two solutions were mixed a deep green color was produced and a white precipitate of magnesium salt appeared. On shaking the mixture, the green color gave way to a bright orange and the mixture became very thick with the solid. After being warmed for one hour and standing at room temperature for several hours, the product was decomposed with water; there was no precipitation

⁷ Schlenk and Thal, *Ber.*, **46**, 2850 (1913).

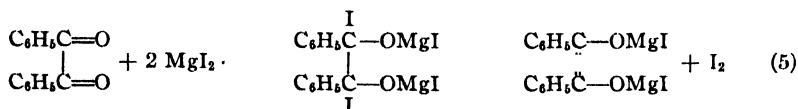
of magnesium hydroxide, showing that reaction was complete. The benzene-ether solution was filtered from a few large, brilliant yellow crystals (triphenylmethyl ether of the unsaturated glycol ?); m. p. 180–190°. From the solution was isolated 2 g. of benzil and the following oxidation and reduction products of triphenylmethyl: 1.5 g. of triphenylcarbinol, 1 g. of triphenylmethane, 0.25 g. of triphenylmethylperoxide. With benzyl chloride and with methyl iodide the glycolate showed no reaction.

Reaction with Bromine and with Iodine.—A solution of 3.43 g. of bromine in 50 cc. of carbon tetrachloride was used for titration of the glycolate from 4.20 g. of benzil and all operations were carried out in an atmosphere of nitrogen. The bromine was absorbed as fast as it was added. A few drops were sufficient to change the yellow color of the bromomagnesium glycolate solution to a dark brown color; further addition produced an opaque brownish-black mixture, and as more bromine was dropped in the solution became lighter in color, going to a transparent red, then to orange and finally to the yellow of benzil solution, which was taken as the end-point. Calcd. for 1 mole of bromine to 1 mole of glycolate: 3.15 g. Found: 3.15 g. Decomposition with water gave 4.00 g. of benzil (95%).

With iodine, instead of titration, the calculated amount of solid iodine was introduced at one time. A considerable amount of heat was generated in the reaction that followed and the solution became opaque brownish-red in color. After half an hour the mixture was translucent, but even after ten days some iodine was still present. Addition of water, followed by the usual separations, gave 94% of the calculated amount of benzil, the other products being benzilic acid, 3%, and benzoin, 1%.

Reaction of Benzil with Magnesium Bromide and with Magnesium Iodide.—Magnesium bromide and benzil form a complex without perceptible change in the yellow color of the solution. By keeping a mixture of 5.25 g. of benzil and 4.5 g. of magnesium bromide in 25 cc. of ether and 35 cc. of benzene in a cool place for two weeks, a large amount of nearly colorless crystals was obtained. The complex was found to have the composition $(C_6H_5CO-COC_6H_5).MgBr_2.(C_2H_5)_2O$. It is readily decomposed by water into its constituents.

The addition of benzil to a solution of magnesium iodide gives rise to a deep red color, occasioned in part by liberation of iodine. A mixture of 4.20 g. of benzil and 5.5 g. of magnesium iodide in 60 cc. of benzene-ether was kept in a dark place for 12 hours. The solution was then poured into water containing a small amount of acid. By titration with sodium thiosulfate 0.32 g. of free iodine was found to be present and there was formed a corresponding amount of magnesium hydroxide. Although the most careful search failed to reveal the least amount of benzoin, we have none the less tentatively assumed the existence of an equilibrium reaction



If oxygen be passed through such a mixture, the glycolate, if actually present, would be fixed as the oxide (VI), thus driving the reaction to the right. Accordingly, dry air was passed through a warm solution of 2.0 g. of benzil and 7.5 g. of magnesium iodide in ether-benzene for two hours. The solution was then hydrolyzed; there were obtained benzil and benzilic acid polymer, 50% of each, and 3.17 g. of iodine was found to be present.

Yet another method suggested itself whereby the assumed reaction could be driven to the right, namely, by removing the iodine by means of some metal other than magnesium. We have found that the addition of molecular silver, of mercury or of zinc actually accomplishes this result and that halomagnesium glycolate is formed in con-

siderable amounts. On hydrolysis yields of benzoin were obtained that corresponded to 55–79% of that possible.

Magnesium bromide, unlike the iodide, gives with benzil no detectable amount of free halogen. Nevertheless, when silver, mercury or zinc is added reaction sets in, in some cases very slowly, and there is produced bromomagnesium glycolate. Hydrolysis resulted in benzoin being formed to the extent of 50–60%.

Benzil with Other Binary Systems.—The binary system Be–BeI₂ with benzil after five days of shaking gave a 95% yield of benzoin on addition of water; the system, Zn–ZnI₂, gave a 71% yield after 22 days. The amount of benzoin indicates the extent of reduction.

Reduction of Benzil by Magnesium Amalgam.—Magnesium alone has no effect on benzil, but in the presence of mercury, which soon coats the magnesium with amalgam, reaction takes place with the production of the usual dark, reddish-brown color. On hydrolysis a 72% yield of benzoin was obtained. Likewise, amalgam prepared by heating together magnesium and mercury was able to reduce benzil.

Mechanism of the Reaction.—The reaction between magnesium, magnesium halide and ketone has been interpreted by us not as a tri-molecular reaction but as one consisting of two bimolecular reactions: (a) a subhalide of magnesium, MgX, is formed; (b) the subhalide adds itself to the oxygen of the carbonyl group. This interpretation we now find fully applicable to the diketone, benzil.

Since benzil, when acted upon by MgX₂ in the presence of silver or mercury, gives the unsaturated halomagnesium glycolate, other interpretations are possible. An unstable addition product may be formed from which the halogen, linked to the carbon atom, is then taken up by the metal directly or through its previous rejection as free halogen (Equation 5).

Considerably more experimental evidence is essential before a final explanation, or explanations, can be advanced as to the mechanism of the reduction accomplished by the various binary systems.

Summary

Benzil in ether-benzene is reduced by the binary systems, Mg–MgI₂ and Mg–MgBr₂, quantitatively to the halomagnesium salt of stilbene-diol, $C_6H_5C(OMgX)=X(MgO)CC_6H_5$.

These unsaturated glycolates were found to be extremely reactive with various reagents; with water benzoin is produced; with acid chlorides esters result; bromine and iodine yield benzil; with oxygen two products are formed, benzil and a polymer of the anhydride of benzilic acid.

Other binary systems were found to reduce benzil in a similar manner. The possible mechanism of the reduction has been discussed.

It may be added that considerable data have been accumulated on the behavior of aliphatic-aromatic ketones, aromatic aldehydes and esters toward the binary systems. The reactions seem to be more complex, though in general of the same nature as described for the ketones.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED KETONES

BY G. H. COLEMAN AND DAVID CRAIG

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Unsaturated aliphatic hydrocarbons react with nitrogen trichloride to form N-dichloro-C-chloro amines. Thus with 2-butene, 2-chloro-3-dichloro-aminobutane is obtained.¹ Reaction will also take place with benzene and toluene but mixtures are obtained which are difficult to separate.²

The present work was carried out in order to study the effect of the presence of the carbonyl group on the addition reactions of nitrogen trichloride and to compare the reaction of nitrogen trichloride on benzalacetophenone with the reaction of phosphorus trichloride on this compound as studied by Conant.³

The reaction of this unsaturated ketone with nitrogen trichloride takes place in carbon tetrachloride solution with the evolution of a large amount of nitrogen, the formation of ammonium chloride, the dichloride of benzalacetophenone and an N-dichloro-C-chloro-amino ketone (I). This compound was first converted into a C-chloro-amino ketone (II) by treatment with concentrated hydrochloric acid. The reducing action of hydrochloric acid on the chloro-amino group was first reported by Berg.⁴

The C-chloro-amino ketone formed by this reaction was isolated as the hydrochloride and on further reduction with sodium amalgam yielded the corresponding amino alcohol (III). The molecular weight of this amino alcohol and that of the corresponding amino ketone, which would have been formed had the ketone group not been reduced, are so nearly the same that a nitrogen analysis does not suitably differentiate between them. Since several acyl derivatives of this compound were found to be oils, the acetylation value was determined with acetic anhydride.⁵

This showed the presence of an hydroxyl group. Since there was the possibility of the formation of a pinacol in the reduction of the ketone,⁶ a molecular-weight determination was made. This indicated that the product was not a pinacol. In order to prove the position of the amino group this amino alcohol was also prepared from the monoxime of dibenzoylmethane by the action of sodium amalgam. This shows Compound III to be a β -amino alcohol, indicating that the chloro-amino

¹ Coleman and Howells, *THIS JOURNAL*, **45**, 3084 (1923).

² Coleman and Noyes, *ibid.*, **43**, 2211 (1921).

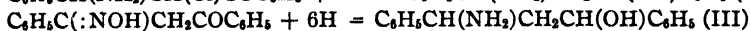
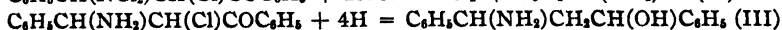
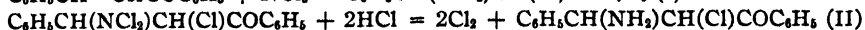
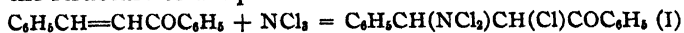
³ Conant, *ibid.*, **42**, 830 (1920).

⁴ Berg, *Bull. soc. chim.*, [3] **7**, 542 (1892).

⁵ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 152.

⁶ Buchka, *Ber.*, **10**, 1714 (1877).

group, in the primary addition, added to the carbon atom farthest from the ketone group. The reactions for the addition and for the proof of the structure of the product are as follows:



No attempt was made to separate racemic mixtures. The preparation of derivatives and the determination of physical properties did not indicate the presence of more than one racemic mixture.

In other addition reactions of benzalacetophenone, where the ketone group is not involved, the negative part of the adding molecule attaches itself to the carbon atom farthest from the carbonyl group. Thus with hydrogen chloride⁷ the chlorine atom goes to the β -position, as does also the cyanide group when hydrogen cyanide⁸ is used. With ammonia and amines⁹ the part containing the nitrogen atom goes to the β -position. This is true of other unsaturated ketones, having been investigated with ammonia and mesityl oxide¹⁰ and particularly well investigated with amines¹¹ and various unsaturated ketones.

While it might be possible to explain the formation of product (I) by a series of reactions following a 1,4 addition to the conjugated system, similar to that which occurs with phosphorous trichloride, it seems more probable that the addition involves only the $-\text{C}::\text{C}-$ linkage, as in the typical addition to unsaturated hydrocarbons.

Experimental Part

The Preparation of the Hydrochloride of 1-Amino-2-chloro-1,3-diphenylpropanone-3.—One hundred and twenty g. of benzalacetophenone was dissolved in 800 cc. of dry carbon tetrachloride in a flask fitted with a mercury-sealed stirrer and connected to a gasometer. The solution was cooled to 0° and 350 cc. of a carbon tetrachloride solution containing 220 mg. moles of nitrogen trichloride was added slowly through a separatory funnel. The nitrogen trichloride was prepared and analyzed by the method described by Coleman and Noyes¹ with the modifications as described by Coleman and Howells.¹

The time required for the addition was about three hours. The evolution of nitrogen began in a few minutes and continued for some time after all of the solution had been run in. The reaction mixture was allowed to stand overnight, during which time it came to room temperature. A small amount of ammonium chloride was filtered off and analyzed. The filtrate contained the dichloride of benzalacetophenone and an N-dichloro-C-chloro-amino ketone and was shaken with 50 cc. of concentrated hydrochloric acid. After 30 minutes, 50 cc. of water was added and the hydrochloride of 1-amino-2-chloro-1,3-diphenylpropanone-3 filtered off. The average yield of the crude

⁷ Rupe and Schneider, *Ber.*, **28**, 957 (1895).

⁸ Hann and Lapworth, *J. Chem. Soc.*, **85**, 1358 (1904).

⁹ Tambor and Wildi, *Ber.*, **31**, 349 (1898).

¹⁰ Sokoloff and Latschinoff, *Ber.*, **7**, 1777 (1874).

¹¹ Kohn, *Monatsh.*, **28**, 423 (1907); *ibid.*, **28**, 461 (1907).

hydrochloride from a large number of runs was about 10%, calculated from the nitrogen trichloride used. This was dissolved in the least possible amount of hot methyl alcohol and precipitated by the addition of a large amount of dry ether. The compound melted with decomposition at 206–208° (uncorr.).

Anal. Subs., 0.1009, 0.1016: 19.96, 19.67 cc. of 0.01634 *N* HCl. Calcd. for $C_{18}H_{14}ClON.HCl$: N, 4.73. Found: 4.53, 4.43.

Subs., 0.1096, 0.1048: 7.45, 7.02 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{18}H_{14}ClON.HCl$: Cl, 23.96. Found: 24.10, 23.76.

Benzoyl-1-amino-2-chloro-1,3-diphenylpropanone-3.—This compound was obtained from the amine hydrochloride by acylation with benzoyl chloride according to the usual Schotten-Baumann procedure. The product after recrystallizing several times from benzene melted at 186–187° (uncorr.).

Anal. Subs., 0.2605: 7.14 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{22}H_{18}ClO_2N$: Cl, 9.76. Found: 9.72.

1-Amino-1,3-diphenylpropanol-3.—Five g. of the hydrochloride was dissolved in 80 cc. of methyl alcohol and 20 cc. of water; 290 g. of 2.5% sodium amalgam was added slowly, with stirring, and with the addition of 6 *N* hydrochloric acid rapidly enough to keep the solution just acid to litmus. The alcohol was boiled off and the free amine extracted from an alkaline solution with ether. The amine was extracted from the ether by 6 *N* hydrochloric acid, the layers were separated and the ether was boiled out of the aqueous layer. The free amine was obtained as a flocculent precipitate by making the solution alkaline. On recrystallizing the product seven times from benzene, the melting point was 122–124° (uncorr.). The product did not contain chlorine, as was shown by the Beilstein test.

Anal. Subs., 0.1254: 5.30 cc. of 0.1038 *N* HCl. Calcd. for $C_{18}H_{17}NO$: N, 6.17. Found: 6.14.

Acetylation Value.—Subs., 0.2422: 2.26 mg. equiv. of acetic anhydride. Calcd. for one OH and one NH_2 , 2.00. Found: 2.12.

Since this value and others similarly obtained were slightly higher than the theoretical, a similar test was made with benzylamine. This gave an acetylation value of 1.10 instead of 1.00. Possibly in both cases a small amount of the diacetylamine compound is formed.

Molecular Weight Determination.—The boiling-point method was used. Subs., 0.3973: 94.0 g. of benzene: boiling-point elevation, 0.053°. Calcd. for $C_{18}H_{17}NO$: 227. Found: 214.

Preparation of the Amino Alcohol from the Monoxime of Dibenzoylmethane.—The monoxime of dibenzoylmethane was prepared according to the method of Wislicenus.¹² It was reduced with sodium amalgam by the same method used in the reduction of the hydrochloride of the aminochloro ketone and yielded the same product; m. p. 122–124° (uncorr.). Mixed melting points showed no depression. Compound (III) is therefore a β -amino alcohol.

Anal. Subs., 0.1229: 5.18 cc. of 0.1038 *N* HCl. Calcd. for $C_{18}H_{17}NO$: 6.17. Found: 6.10.

Summary

1. The reaction of nitrogen trichloride with benzalacetophenone in carbon tetrachloride solution has been shown to form among other products 1-dichloro-amino-2-chloro-1,3-diphenylpropanone-3. The addi-

¹² Wislicenus, *Ann.*, **308**, 250 (1899).

tion is probably a simple addition to the —C=C— bond and does not involve the ketone group.

2. This compound was reduced to 1-amino-2-chloro-1,3-diphenylpropanone-3 by concentrated hydrochloric acid and on further reduction with sodium amalgam 1-amino-1,3-diphenylpropanol-3 was obtained.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,
No 556]

A QUANTITATIVE STUDY OF THE INFLUENCE OF SODIUM ACETATE, SODIUM BORATE, SODIUM CITRATE AND SODIUM PHOSPHATE UPON THE ACTIVITY OF PANCREATIC AMYLASE

BY H. C. SHERMAN, M. L. CALDWELL AND JANE E. DALE

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In continuation of our study of the nature and properties of pancreatic amylase it became important to obtain further quantitative information on the influence of electrolytes upon its action. The first series of experiments described briefly here deal with the sodium salts of acetic, boric, citric and phosphoric acids.

Data dealing with the influence of these salts upon enzymic activity have been reported from time to time by various investigators but unfortunately they are conflicting and hard to interpret because of failure to recognize the simultaneous importance of other factors such as the hydrogen-ion activities of the solutions, the concentrations of substrates and electrolytes and the value of strictly comparable data obtained under parallel conditions.

Experiments were, therefore, planned in which each of these factors was carefully considered.

Experimental

The general plan was to study the influence upon the amylase activity, of each salt alone in solutions in which the hydrogen-ion activities differed at close intervals (by about 0.1 Ph) and then to make a quantitative parallel comparison of the influence of the different salts, the solutions being adjusted in each case to the hydrogen-ion activity which had been found to favor the optimal activity of the enzyme in the presence of that salt.

The same preparation of pancreatin was used throughout and its activity measured under constant conditions, half-hour hydrolyses of 2% starch at 40°. The hydrogen-ion activity of each starch solution used was measured electrometrically at room temperature.

As has been shown in earlier papers from this Laboratory,¹ amylase

¹ Sherman and co-workers, *THIS JOURNAL*, 32, 1073, 1087 (1910); 33, 1195 (1911); 34, 1104 (1912); 35, 1617, 1784 (1913); 37, 623 (1915); 41, 231 (1919); 43, 2461 (1921).

activity may be measured quantitatively by determining, under carefully controlled conditions, the increase in the reducing action of the hydrolysis mixture caused by the formation of reducing sugar from the starch by the enzyme. The details of the method will not be repeated here.

All salts were recrystallized and air-dried. Sodium acetate, tertiary sodium citrate and mono- and disodium phosphates were used as such. Sodium borate was obtained in the starch solutions by adding recrystallized boric acid and adjusting the hydrogen-ion activities with 0.01 *M* sodium hydroxide. The influence of the salts was measured in the presence of 0.05 *M* sodium chloride.

Discussion of Results

Experiments with Sodium Phosphate.—The total concentration of sodium phosphate in the solutions was varied from 0.0005 to 0.05 *M* and the hydrogen-ion activities were adjusted by the use of suitable proportions of equimolar solutions of mono- and disodium phosphate. The activity of pancreatic amylase was found to be independent of these concentrations of phosphate provided the hydrogen-ion activities of the solutions were suitably adjusted to *P_H* 7.0 to 7.2 for the lower concentrations and to *P_H* 7.0 for solutions containing 0.05 *M* sodium phosphate. A concentration of 0.004 *M* was chosen as suitable for the comparison of sodium phosphate with the other salts studied.

Experiments with Sodium Citrate.—In the presence of 0.004 *M* sodium citrate the enzyme was found to exert its optimal activity in solutions of *P_H* 7.0 to 7.2. Direct comparisons showed that the amylase was practically as active in the presence of citrate as in the presence of phosphate

Experiments with Sodium Acetate.—As this salt is not effective as a buffer in solutions of about *P_H* 7.0 it was difficult to control the hydrogen-ion activities of the solutions as accurately as is desirable for work with enzymes. The data obtained, however, indicate no marked difference in the influence of acetate and phosphate upon pancreatic amylase. In comparable experiments, the activity of the enzyme although more irregular was nearly if not quite as high in the presence of acetate as in the presence of phosphate and the differences and irregularities in the results with the acetate solutions can readily be explained by slight departures from the optimum conditions in the less adequately buffered solutions.

Experiments with Sodium Borate.—Experimental difficulties in controlling the hydrogen-ion activities of the solutions containing sodium borate were also encountered, and probably here too because the solutions were inadequately buffered. It was found, however, that when the solutions were adjusted to about *P_H* 7.0, ten-fold variations in the borate concentration from 0.001 *M* to 0.01 *M* did not influence the activity

of the enzyme and that the activity of the enzyme, in the presence of borate, while less regular and slightly lower, was within the experimental limits of its activity in the presence of phosphate.

Experiments in the Absence of any "Buffer" Salt.—A further comparison of the activity of pancreatic amylase in solutions with and without phosphate was made. The hydrogen-ion activities were adjusted in one series of solutions with phosphate and in the other with sodium hydroxide, no phosphate being added. Sodium chloride, 0.05 *M*, was present in both series. The results in the unbuffered solutions were more irregular and the activity of the enzyme was often, but not always, slightly lower than in the presence of phosphate. The results as a whole indicate that the addition of phosphate to the substrate aids the enzymic activity by its favorable influence in helping to control the hydrogen-ion activities of the solutions rather than because of any "specific" influence of the phosphate itself.

Conclusions

The activity of pancreatic amylase in the presence of 0.05 *M* sodium chloride and under optimal conditions of hydrogen-ion activity is practically the same in the presence of equimolar concentrations of citrate and phosphate. It is slightly lower in the presence of borate and acetate but this decrease in activity seems to be more probably due to less adequate control of hydrogen-ion activity in the less adequately buffered solutions rather than to any specific effect of the acetate or borate ions.

When acting in the presence of 0.05 *M* sodium chloride and 0.004 *M* concentrations of the sodium salts of boric, citric and phosphoric acids for half-hour periods at 40°, pancreatic amylase exerts its optimum activity in solutions of *PH* 7.0 to 7.2.

In the presence of 0.05 *M* sodium chloride the activity of the enzyme appears to be independent of the concentrations of phosphate from 0.0005 to 0.05 *M* and of borate from 0.001 to 0.01 *M* provided the optimal conditions of hydrogen-ion activity are maintained.

Given optimal hydrogen-ion activity, the activity of the enzyme appears to be practically the same in starch solutions containing 0.05 *M* sodium chloride and no phosphate, as it is in solutions containing phosphate as well.

In view of the fact that the activity of the enzyme in the absence of any salt except sodium chloride may be as great as in the presence of phosphate and that the activity is practically the same in the presence of acetate, borate, citrate or phosphate, it seems improbable that these salts have any marked specific effect upon the enzyme.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DIFFERENTIAL CLEAVAGE OF THE CARBON TO CARBON LINKAGE BY ALKALI METALS

BY J. B. CONANT AND B. S. GARVEY, JR.

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Schlenk¹ has shown that dissociable ethanes such as hexaphenylethane react with one per cent. sodium amalgam, forming such colored sodium compounds as triphenylmethyl sodium. Later Ziegler² found that the action of the liquid sodium-potassium alloy was so vigorous that even tetraphenylethane was cleaved with the formation of potassium diphenylmethyl. Like the other metallic derivatives this reacted with water, yielding the methane, and with carbon dioxide, forming the salt of diphenylacetic acid.

In a previous paper³ we have reported the use of Ziegler's reagent in preparing xanthanoic acid from dixanthyl. As would be expected, a similar reaction takes place between the substituted dixanthyls and the alloy.⁴ The acids prepared from metallic derivatives from four substituted dixanthyls are reported in the experimental portion of this paper.

Although dibenzyl dixanthyl at 25° absorbs oxygen as rapidly as a dissociated ethane, it does not react with one per cent. amalgam in dry ether or benzene even on 24 hours' shaking at room temperature. Under the same conditions in either solvent hexaphenylethane gives a bright red color in five minutes, due to the formation of the metallic derivative. At 80° a solution of dibenzyl dixanthyl begins to show a color which fades on cooling. This fact together with its extreme reactivity toward oxygen makes it evident that at room temperature it is either somewhat dissociated in solution or a number of the molecules are in a reactive state closely akin to "real" dissociation. Yet one per cent. sodium amalgam serves to differentiate this compound from hexaphenylethane, which is about 20% dissociated in a dilute solution at 80° and only slightly dissociated at room temperature.⁵

In the hope of finding other reagents that would differentiate between carbon linkages of varying reactivity, we studied 40% sodium amalgam, which is also a liquid at 25°. This reagent reacts with hexaphenylethane and the substituted dixanthyls listed in Table I at room temperature in both ether and benzene. It reacts with dixanthyl at an appreciable rate only in ether and does not react at all with tetraphenylethane.

¹ Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

² Ziegler and Thielmann, *Ber.*, **56B**, 1740 (1923).

³ Conant and Garvey, *THIS JOURNAL*, **49**, 2080 (1927).

⁴ Conant and Sloan, *ibid.*, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925). Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

⁵ Gomberg, *Chem. Reviews*, **1**, 107 (1924).

Table I summarizes a series of experiments carried out for the purpose of comparing the reactivity of certain ethanes and dixanthyls. The conditions were as nearly the same as possible in all the experiments and the results are therefore strictly comparable. It is evident that by the use of sodium-potassium alloy and the two liquid sodium amalgams in either benzene or ether it is possible to differentiate between hexaphenylethane, the substituted dixanthyls (with primary groups), dixanthyl, tetraphenylethane and dibenzyl. The differentiation is sharp although it is undoubtedly a question of relative rates of reaction. Thus, although the substituted dixanthyls showed no color with one per cent. amalgam in five minutes or in 24 hours, after many days of continuous shaking a reddish color developed.

TABLE I
THE CLEAVAGE OF CERTAIN COMPOUNDS BY ALKALI METAL

Substance	Na-K ether	Na-K C ₆ H ₆	40% Na-Hg ether	40% Na-Hg C ₆ H ₆	1% Na-Hg ether	1% Na-Hg C ₆ H ₆
Hexaphenylethane	+	+	+	+	+	+
Dibenzyl	+	+	+	+	—	—
Di- <i>n</i> -butyldixanthyl	+	+	+	+	—	—
Diethyldixanthyl	+	+	+	+	—	—
Dimethyldixanthyl	+	+	+	+	—	—
Dixanthyl	+	+	+	—	—	—
Tetraphenylethane	+	+	—	—	—	—
Dibenzyl	—	—	—	—	—	—

A + sign indicates appreciable cleavage in five minutes as judged by appearance of red color.

A — sign indicates no cleavage in five minutes.

In each case 0.00025 mole of the ethane in 5 cc. of the solvent was shaken with 1 cc. of the liquid metal. The tubes were all shaken violently by hand for five minutes.

The Rate of the Cleavage Reaction Using Sodium-Potassium Alloy

The rate of the cleavage reaction may be followed by either of two methods which give only approximate results. The potassium derivative may be decomposed with carbon dioxide and the resulting acid isolated and weighed. A more rapid method is to titrate the mixture with moist benzene until the color of the metallic derivative disappears. In both methods separate tubes must be used for each time interval. A comparison of the amount of cleavage determined by the two methods with dixanthyl and with tetraphenylethane gave results as follows: (a) dixanthyl fast shaking five min., by carbon dioxide 23%, by titration, 13%; (b) dixanthyl 50 minutes' slow shaking (on a machine), by carbon dioxide 14%, by titration 4.4%; (c) tetraphenylethane 250 minutes' shaking, by carbon dioxide 55%, by titration 45%. The rate of shaking is very important as the results with dixanthyl show and as others with diethyldixanthyl demonstrated; rapid shaking by hand is more effective than the slow

shaking of the shaking machine. The amount of alloy and the concentration of the solution are also important. Thus a solution of 0.09 g. of dixanthyl in 5 cc. of ether with 0.25 cc. of alloy required four minutes' shaking for the development of color, with 0.5 cc. of alloy twenty seconds' and with 1 cc. of alloy five seconds'. Because of these variable factors which can be only partially controlled, exact data on the rates of this heterogeneous reaction could not be obtained. In all the comparative experiments we took pains to use the same size and shape of tubes, the same concentration of materials, the same amount of liquid alloy (or amalgam) and to shake in the same manner.

The rates of cleavage of dixanthyl, dimethyldixanthyl, diethyldixanthyl and dibutyldixanthyl were compared using sodium-potassium alloy (1 cc.) and 10 cc. of a 0.025 molar solution. The rate was followed by the titration method and while duplicate determinations in many cases showed considerable divergence the general course of the reaction was evident. (The numerical results are given in the experimental portion of the paper.) Interesting enough, these substances (except dimethyldixanthyl) reacted with sodium-potassium alloy in ether at approximately the same rate. The dimethyldixanthyl reacted at about the same rate as the others during the first five minutes but then the rate fell off rapidly and after 250 minutes only 25% had reacted. It seems probable that with this substance some irreversible rearrangement or decomposition may have been catalyzed by the alloy, and that three-quarters of the material may have been transformed before it had an opportunity of reacting. The reaction of these same compounds with 40% sodium amalgam was so slow that no reliable figures could be obtained; the indications were that the dialkyl dixanthyls reacted about ten times as rapidly as the parent substance.

There might seem to be an inconsistency between the results given in Table I and those mentioned in the preceding paragraph. Forty per cent. sodium amalgam acting on a benzene solution differentiates clearly between dixanthyl and the primary alkyl derivatives. Yet the rates of cleavage by the alloy in ether are not appreciably different. We interpret these results as showing that in the reaction with the alloy the rate-determining process is physical and not chemical, and that only with the 40% amalgam does the difference in reactivity of the compounds manifest itself. It is evident that no heterogeneous reaction involving the mixing of two liquid phases will be likely to proceed instantaneously. The rate will depend on the diffusion of material at the boundary where the reaction proceeds. This rate will be affected by relative volumes, method of mixing and concentrations, as has been noted in our experiments.

The rate of the reaction may also be determined by the solubility of the product and its tendency to cling to the metallic globules. Therefore,

the results obtained by using a graded series of reagents (Table I) would be expected to yield more information regarding the rate of the *chemical* reaction than the experiments with sodium-potassium alloy alone.

Experimental

The Formation of Substituted Xanthanoic Acids by Cleavage of Substituted Dixanthyls

One gram of the substituted dixanthyl in 100 cc. of absolute ether was shaken with 10 cc. of sodium-potassium alloy in an atmosphere of nitrogen for 16 hours. The red solution containing a red precipitate was treated with dry carbon dioxide, the alloy removed and the ether layer extracted with water. The aqueous layer was acidified and the precipitated acid purified by recrystallization, usually from a mixture of methyl alcohol and water. The physical properties and analysis of the acids obtained in this way are given in Table II. The methyl esters (also given in Table II) were prepared by the action of dimethyl sulfate on the alkaline solution.

TABLE II

Compound	Prepared from	M p °C.	Found % C		Found % H		Equivalent weight by titration, NaOH		Molecular weight in freezing benzene	
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Methylxanthanoic acid	Dimethyl-dixanthyl	205 206	74.8	75.0	5.3	5.0	235	240
Methyl ester of methyl xanthanoic acid	The acid	96 97	76.1	75.6	5.6	5.5	239	254
Ethylxanthanoic acid	Diethyl-dixanthyl	173-174	75.9	75.6	5.7	5.5	252	254
n-Butylxanthanoic acid	Di-n-butyl-dixanthyl	144 145	76.6	76.6	6.5	6.4	286	282
Methyl ester of n-butyl xanthanoic acid	The acid	73-74	77.0	77.0	7.2	6.8	280	296
Benzylxanthanoic acid	Dibenzyl-dixanthyl	232	79.7	79.7	5.6	5.1	319	316
Methyl ester of benzyl-xanthanoic acid	The acid	103 104	80.0	80.0	6.0	5.5	314	330

Determination of the Rate of Cleavage

The solution of the material under investigation and the alloy were placed in glass tubes of 15-20 cc. capacity. These were sealed off after filling with dry, oxygen-free nitrogen. (The final purification of the nitrogen consisted in passing it through a solution of sodium triphenylmethyl in ether at 0°.) After shaking (at $23 \pm 3^\circ$) the tube was placed in a larger cylindrical container of stout glass. This was filled either with dry carbon dioxide or the purified nitrogen, depending on whether the acid was to be isolated or the metallic derivative was to be titrated. By a sharp shake the tube containing the reaction mixture could be broken (a file scratch at the shoulder near the constriction facilitated this operation).

In the titration experiments moist benzene was run in from a buret, the end-point being the disappearance of color. The moisture reacts so much more rapidly with the metallic derivatives than with the alloy that the presence of the latter did not seriously interfere. The benzene was saturated with water at a definite temperature and the solubility of water in benzene as given in Seidell's⁶ tables was used in the calculation.

⁶ Seidell, "Solubilities of Organic and Inorganic Compounds," D. Van Nostrand Company, New York, 1919.

In the experiments reported below, 1 cc. of the liquid metal and 10 cc. of the solvent containing 0.00025 mole of the substance were used. All of the tubes were of the same size. They were shaken violently for 30 seconds to disperse the metal and then on the shaking machine for the time indicated. The calculation of the per cent cleavage from the data is illustrated by the following typical run: 0.09 g. of dixanthyl, 10 cc. of ether, 1 cc. of sodium-potassium alloy, shaken 50 minutes, 6.5 cc. of benzene saturated with H_2O at 23° required; theoretical cc. for complete cleavage 16.7 (at 23° 100 cc. of benzene holds 53.7 mg. of water); per cent. cleaved, 39.0.

Rate of cleavage of **dixanthyl**. With sodium-potassium alloy in ether (the numbers are the per cent. cleavage): 5 min., 39.0, 42.0; 125 min., 71.8, 77.8. With 40% sodium amalgam: 125 min., 1.2; 250 min., 1.4, 1.4. With sodium-potassium alloy in benzene: 250 min., 6.0, 6.8. With 1% amalgam in ether or 40% amalgam in benzene, no perceptible cleavage in 250 min.

Rate of cleavage of **dimethyldixanthyl**. With sodium-potassium alloy in ether: 5 min., 6.2, 6.2; 50 min., 8.6, 12.3; 125 min., 14.2, 16.6; 250 min., 23.3, 24.6. With sodium-potassium alloy in benzene, 250 min., 5.2, 5.2. With 40% amalgam in ether, 250 min., 1.2, 2.0. With 1% amalgam, none in 250 min.

Rate of cleavage of **diethyldixanthyl**. With sodium-potassium alloy in ether: 5 min., 9.9, 15.7; 50 min., 51.1, 47.1; 125 min., 59.9, 69.7. With sodium-potassium alloy in benzene: 125 min., 4.8; 250 min., 5.5, 7.2. With 40% amalgam in ether: 125 min., 3.1; 250 min., 4.9, 10.5. With 40% amalgam in benzene: 250 min., 1.4, 4.8. With 1% amalgam, none in 350 min.

Rate of cleavage of **di-n-butyldixanthyl**. With sodium-potassium alloy in ether: 5 min., 1.7, 4.1; 50 min., 42.0, 47.5; 125 min., 63.6, 73.3. With sodium-potassium alloy in benzene: 125 min., 4.2; 250 min., 6.0, 7.5. With 40% amalgam in ether: 125 min., 3.1; 250 min., 2.7, 7.4. With 40% amalgam in benzene: 250 min., 5.5, 6.0. With 1% amalgam in ether, none in 330 min.

Summary

1. The action of sodium-potassium alloy, 40% sodium amalgam and 1% sodium amalgam on a number of substituted dixanthyls and certain ethanes has been studied. By using these reagents in benzene or ether one can differentiate between certain compounds which contain a reactive carbon to carbon linkage.

2. The rate of cleavage by sodium-potassium alloy is essentially the same for a number of substituted dixanthyls and dixanthyl itself. This is probably due to the fact that with this powerful reagent a physical process controls the rate of the heterogeneous reaction.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

A COMPARISON OF HETEROCYCLIC SYSTEMS WITH BENZENE

II. REDUCTION POTENTIALS OF QUINONES CONTAINING THE PYRIDINE, IMIDAZOLE, TRIAZOLE AND THIOPHENE RINGS

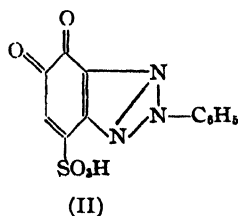
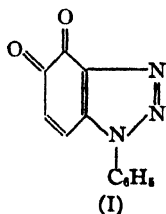
BY LOUIS F. FIESER AND MARION A. AMES

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In the first paper of this series¹ a description was given of an experimental method of studying various unsaturated ring systems which consists in comparing, by means of oxidation-reduction potential measurements, the oxidizing power of a compound such as α -naphthoquinone, in which a benzene ring is fused to a quinone grouping, with the oxidizing power of a quinone formed by replacing the benzene ring of α -naphthoquinone by a heterocyclic nucleus. The relative extent to which the reduction potential of benzoquinone is decreased by the attachment of the benzene ring and of the heterocycle furnishes a means of characterizing quantitatively the relationship between the two cyclic systems.

The interpretation of the results of such a study would be greatly simplified if it were possible to obtain and perform measurements with simple heterocyclic analogs of the naphthoquinones; but it appears that, in the case of certain heterocycles, this is very difficult if not impossible. Both 4,5-indazolequinone¹ and, as we have now found, 1-phenylbenzotriazole-4,5-quinone(I)² undergo decomposition too rapidly to permit of satisfactory e.m.f. measurements in alcoholic solution. The destruction of these quinones is undoubtedly due to the 1,4 addition of solvent, acid or a second quinone molecule to the conjugated system, and it can often be prevented by the introduction of a sulfonic acid group in the reactive 4 position. Thus 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid (II)



which was synthesized from 2-phenyl-5-hydroxybenzotriazole was, like indazolequinone sulfonic acid, well suited to the purpose at hand. We were unable, however, to obtain the corresponding 1-phenyltriazole derivative. Unlike many similar *o*-quinones, 1-phenylbenzotriazole-4,5-quinone (I) does not react with sodium bisulfite, so that the direct

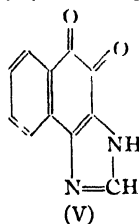
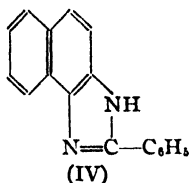
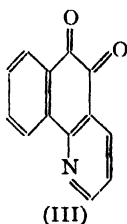
¹ Fieser, *THIS JOURNAL*, **48**, 1097 (1926).

² Fries and Empson, *Ann.*, **389**, 345 (1912).

preparation of the sulfonated hydroquinone could not be accomplished. It was found, moreover, that although 1-phenyl-5-hydroxybenzotriazole readily couples with diazonium salts, it fails to yield a nitroso derivative with nitrous acid, so that the convenient reaction of *o*-nitrosophenols could not be utilized. Further obstacles encountered in the 1-phenyl-triazole series are recorded in the Experimental Part.

In view of this experience and because difficulties in the synthesis of other heterocycles were anticipated, it seemed advisable at this time to determine to what extent some of the more readily available heterocyclic quinones would serve to furnish the desired comparison with benzene. To this end a given compound must be at least slightly soluble in alcohol or water, it must be stable in solution and undergo strictly reversible reduction. It is essential, moreover, that sufficient data for related compounds are available in order to interpret the results adequately. In the present study we have examined several known quinones and two new ones from the experimental standpoint and we expect to supply in the future such additional data as now appear necessary for a proper evaluation of some of the results.

Samples of 2-phenyl- α,β -naphthotriazole-4,5-quinone (VI, below)³ and the isomeric 3-phenyltriazole derivative⁴ were kindly furnished for this investigation by Professor Charrier, to whom we wish to express our sincere thanks. Since these compounds, as well as the 1-phenyltriazole isomer,⁵ were obtained by the oxidation of the tricyclic analogs of phenanthrene, and since α -naphthoquinolinequinone (III) has been prepared by the oxidation of α -naphthoquinoline,⁶ it might be expected that a number of other quinones could be obtained in a similar manner. It appears, however, that the method is not one of very general application.



While α,β -naphthotriazole-4,5-quinone (VIII, below)⁷ was readily prepared by the oxidation of α,β -naphthotriazole, no products possessing the properties of a quinone were obtained by the oxidation of 2-methyl- α,β -naphthimidazole⁸ or 2-phenylnaphthimidazole (IV).⁸ Skraup and

³ Charrier, *Gazz. chim. ital.*, **54**, 610 (1924).

⁴ Charrier, Beretta and Gisella, *ibid.*, 56, 191 (1926).

⁵ Charrier, *Atti accad. Lincei*, (VI), 4, 312 (1926).

* Skraup and Cobenzl, *Monatsh.*, **4**, 461 (1883)

⁷ Zincke and Noack, *Ann.*, 295, 1 (1897).

⁸ Fischer, *Ber.*, **34**, 935 (1901)

Cobenzl⁶ attempted to convert β -naphthoquinoline into the corresponding quinone but found that oxidation always involved cleavage of the central ring; the experience of Beretta⁹ with 2-phenyl-5,6-quinolinetriazole was entirely similar. Although few of the corresponding linear tricyclic compounds appear to have been studied, Fries and Empson report a similar failure to convert N-diphenyl-diethenyl-1,2,4,5-tetra-aminobenzene into a quinone by direct oxidation.²

Another method of synthesizing analogs of phenanthrenequinone utilizes 1,2-dihydroxy-3,4-diaminonaphthalene as the starting material.⁷

TABLE I
NORMAL REDUCTION POTENTIALS AT 25°

Compound	Solvent	E_0 , v. —			ΔE_1 , mv.	ΔE_2 , mv.	E_0 (Av.) v.
2-Phenylbenzotriazole-4,5-quinone-7-sulfonic acid (II).....	0.1 N HCl	0.643	0.642		23	18	
	1.0 N HCl	.644	.644	0.645	19	17	0.644
2-Phenyl- α,β -naphthotriazole-4,5-quinone (VI).....	50% alc.	.469 .471	.470	.471	18	25	.470
3-Phenyl- α,β -naphthotriazole-4,5-quinone (VII).....	50% alc.	.514	.512	.514	18	18	.513
α,β -Naphthotriazole-4,5-quinone (VIII) .	0.1 N HCl	.466 .465	.464	.465	25	21	.465
	1.0 N HCl	.477	.476		21	24	.477
α -Naphthoquinolinequinone (III) ¹⁰	0.1 N HCl	.554	.554		21	20	.554
	1.0 N HCl	.560	.560		18	17	.560
	50% alc.	.565	.563		18	19	.564
α,β -Naphthimidazole-4,5-quinone (V)....	50% alc.	.529 .527	.527	.527	17	19	.528
Phenanthrenequinone ¹¹	0.1 N HCl	.442 .439	.443	.443	29	23	.442
	50% alc.	.458	.459	.458	17	19	.458
1-Phenyl- β,β -naphthotriazole-4,9-quinone (X) ¹²	50% alc.	.259	.256	.253	158	41	(.256)
1-(<i>p</i> -Tolyl)- β,β -naphthotriazole-4,9-quinone (XI) ¹³	50% alc.	.241 .246	.245	.243	63	48	(.244)
2-Methyl-3-phenyl- β,β -naphthimidazole-4,9-quinone (XII) ¹⁴	50% alc.	.319	.322	.318	23	23	.320
Thionaphthenequinone (XVIII) ¹⁵	0.1 N HCl	.263	.264	.264	18	19	.264
Thiophanthrenequinone (XX) ¹⁶	50% alc.	.250	.250	.249	19	19	.250

⁹ Beretta, *Gazz. chim. ital.*, **57**, 179 (1927).

¹⁰ M. p., 206°. Skraup and Cobenzl, Ref. 6.

¹¹ The value of 0.471 v. for the reduction potential in 95% alcohol, 0.5 N in hydrogen chloride, determined by Conant and Fieser, *THIS JOURNAL*, **46**, 1858 (1924), was also verified.

¹² M. p., 242°. Fries and Billig, *Ber.*, **58**, 1128 (1925).

¹³ M. p., 208°. Ref. 12.

¹⁴ M. p., 237°. Ref. 12.

¹⁵ M. p., 116°. Friedländer, *Ann.*, **351**, 399 (1907).

¹⁶ M. p., 227–228°. Steinkopf, *Ann.*, **407**, 99 (1915). The yield of *o*-2-thenoylbenzoic acid was increased to 43% by the use of 2.2 equivalents of aluminum chloride in the Friedel and Crafts reaction.

By condensing this substance with formic acid and oxidizing the product, α,β -naphthimidazole-4,5-quinone (V) was readily obtained.

Determinations of the reduction potentials of the quinones which have been mentioned, and of certain others which are described in the literature, were carried out by electrometric titration with titanous chloride. A hydrogen electrode containing some of the solvent which was used to dissolve the quinone formed the reference half-cell. Measurements were made when possible in aqueous solution, but in most cases the solvent employed was 50% alcohol containing 0.1 mole of hydrogen chloride and 0.2 mole of lithium chloride per liter, the latter electrolyte being added to increase the conductivity of the solution. Though most of the compounds studied dissolve only to a very slight extent in this solvent, no difficulty was experienced in working with the dilute solutions. The results are summarized in Table I. The term "50% alcohol" is used to signify the solution described above. Values found for the normal reduction potentials by interpolation of the titration curves at the point corresponding to half-reduction are given under the heading E_0 , while under ΔE_1 and ΔE_2 are given the average differences between E_0 and the potentials at 20% and 80% reduction, respectively. The theoretical value is 17.8 millivolts.

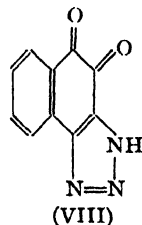
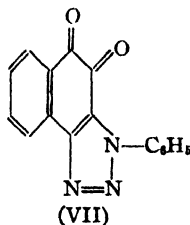
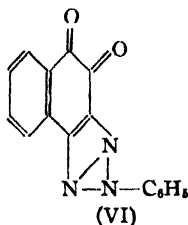
In considering the results, attention may first be called to the fact that the potentials of some of the quinones containing nitrogen increase with increasing acidity of the solution. The variation is probably due to changes in the extent of the basic dissociation of the organic substances.¹⁷ The normal reduction potentials referred to the undissociated oxidant and reductant, which we regard as the most significant for the purpose of correlating reduction potentials and structure, are probably somewhat lower than the values obtained for 0.1 *N* hydrochloric acid and cannot now be accurately evaluated. In view of this uncertainty, too great significance should not be attached to the exact values of the "normal potentials" of those compounds whose potentials change with acidity. Thus the potential of α -naphthoquinolinequinone in 0.1 *N* hydrochloric acid is 0.112 v. higher than that of phenanthrenequinone, but the variation with acidity indicates that the difference between the potentials would be less in a solution of such acidity that no dissociation could occur. While it seems unlikely that such a large difference can be due entirely to the effect of ionization, and while the present results thus point to a surprising difference between the pyridine and the benzene nucleus, it is best to reserve judgment on this point until further data are available.

In the case of the phenyltriazole derivatives there is evidence that the results are not influenced by ionization, for the potential of the sulfonated quinone, II, is independent of the acidity of the solution. More

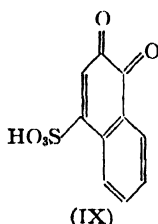
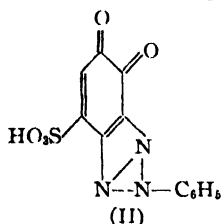
¹⁷ Clark and Cohen, *Pub. Health Repts.*, **38**, 666 (1923).

confidence can thus be placed in the values for this compound and for those similarly constituted.

It will be observed that the values for the normal reduction in 50% alcoholic solution of 2-phenyl- α,β -naphthotriazole-4,5-quinone (VI) and for phenanthrenequinone are very nearly the same. The substitution of the 2-phenyltriazole nucleus for one of the benzene rings in phenanthrenequinone thus produces an alteration in the reduction potential that is scarcely perceptible, which indicates a close relationship between



the two cyclic systems. It is important that the same conclusion may be inferred from entirely independent data; the reduction potential of 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid (II) in aqueous solution is 0.643 v.; that of 1,2-naphthoquinone-4-sulfonic acid (IX) is 0.630 v.



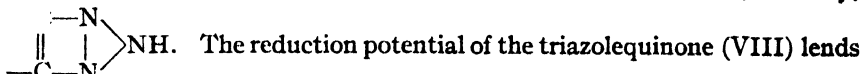
That the potentials of the benzenoid quinone and the heterocyclic quinone differ by almost exactly the same amount here as in the tricyclic series is excellent evidence of the general validity of the method and indicates that phenanthrenequinone may be taken as a standard for comparison even though the relationship of the potential to that of β -naphthoquinone is not yet understood.¹⁸

While 2-phenyl- α,β -naphthotriazole-4,5-quinone (VI) is very similar in potential to phenanthrenequinone, the value for the 3-phenyl isomer (VII) differs by the considerable quantity of 0.047 v. The results for the three

compounds indicate that the 2-phenyltriazole system, $\begin{array}{c} \text{---C---N---} \\ || \quad | \\ \text{---C---N---} \end{array} \text{N---R,}$ like the benzene ring, represents a condition of greater stability, or of less reactivity and unsaturation, than the isomeric grouping, $\begin{array}{c} \text{---C---N---R} \\ || \quad \diagup \\ \text{---C---} \end{array}$.

¹⁸ Conant and Fieser, *THIS JOURNAL*, **46**, 1858 (1924).

On the basis of this evidence, it seems likely that the unsubstituted triazoles, which can conceivably correspond in structure to either of the phenyl derivatives, have the structure of the more stable isomer, namely,



some support to this conclusion, for it approaches more closely that of the 2-phenyl derivative than that of the isomer. Moreover, since a phenyl group lowers somewhat the potential of benzoquinone,¹⁹ it would be expected that the potential of the true phenyl derivative of naphthotriazolequinone would be perhaps lower, but surely not higher, than that of the parent compound. This relationship is maintained only if the above structure for the triazole ring is adopted.

This structure for the 1,2,3-triazoles was first advanced by Griess,²⁰ though Zincke²¹ showed that the evidence was unsatisfactory. On the other hand, the evidence which led Zincke to favor the double-bond structure does not now appear to exclude definitely the Griess formula.²² The present results indicate that a reexamination of this problem is desirable.

Though it is too early to consider the matter in detail, it is of interest to compare briefly our results in the triazole series with those of other investigators. Zincke²³ found that many benzotriazole derivatives were hardly distinguishable from the corresponding naphthalene compounds; Fries,²⁴ by the extensive application of more definite comparative methods, concluded that the two isomeric phenyl derivatives are exactly similar to each other and to naphthalene. The present work supports these conclusions in a general way, though it points to a difference between the phenyltriazoles. It is of course possible that the electrochemical method reveals differences which are too slight to be detected by a study of the course of substitution reactions; but in view of our results for the pyrazole nucleus¹ and the tentative results for pyridine, it seems more probable that the two methods do not furnish precisely the same information concerning the character of the ring systems in question. For one thing, our method is concerned solely with equilibria, while most of

¹⁹ Private communication from Dr. J. B. Conant.

²⁰ Griess, *Ber.*, **15**, 1878 (1882).

²¹ Zincke, *J. prakt. Chem.*, [2] **53**, 97 (1896).

²² A third possible structure for benzotriazole, as well as for its 2-N substitution products, involves the "oso-triazole," or quinone-di-imine grouping. Fries, however, has recently shown (*Ann.*, **454**, 137 (1927)) that this structure is inconsistent with the properties of these substances.

²³ Zincke, *Ann.*, **311**, 277 (1900).

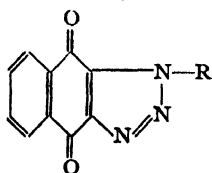
²⁴ (a) Fries, *Ann.*, **389**, 305 (1912). (b) Fries and Roth, *ibid.*, **389**, 318 (1912). (c) Fries and Empson, *Ref. 2*. (d) Fries, Sudhoff and Brettschneider, *ibid.*, **454**, 131 (1927).

the methods employed by Fries depend largely upon the relative rates of competing reactions.

It is of interest that Charrier's statement⁴ that 2-phenyl- α,β -naphthotriazole-4,5-quinone is more closely related to phenanthrenequinone in physical properties than the 3-phenyl isomer corresponds with the electrochemical results.

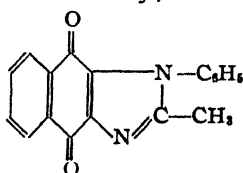
Our results have some bearing on the anomalous relationship between the potentials of some of the benzenoid quinones.¹⁸ Since the attachment of a phenylene group to *o*-benzoquinone lowers its potential by 0.222 v., two such groups would be expected to lower the potential by 0.444 v.; the actual value is considerably less, namely, 0.335 v. In the same way it may be calculated that the attachment of a phenylene group and a 2-phenyltriazole group to *o*-benzoquinone should lower its potential by 0.431 v., if the effects are additive; but the actual value is 0.313 v. The relationship between the compounds of the bi- and tricyclic series is thus the same whether or not one ring is heterocyclic, and it seems probable at the present time that the position of phenanthrenequinone on the potential scale is due to the angular structure of the compound rather than to some peculiar property or structure of the benzene rings of the quinone or its reduction product.

It is important to determine if a similar situation obtains in the series of the linear tricyclic substances such as anthraquinone and its heterocyclic analogs. Unfortunately, the results with the triazole derivatives, X and XI, are not altogether satisfactory; the value for X



X(R = $-\text{C}_6\text{H}_5$)

XI(R = $-\text{C}_6\text{H}_4\text{CH}_3$)

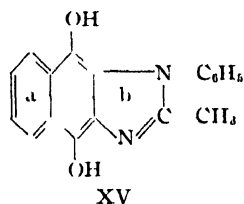
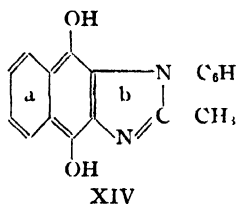
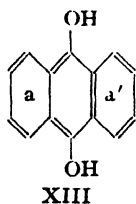


XII

may be as much as 10 mv. too high; that for XI is probably accurate to within 5 mv. However, there can be little doubt as to the general position of the potentials of these compounds, and they may be compared with that of anthraquinone, which is 0.155 v. If compound X were related to anthraquinone in the same way that the angular isomer VII, which also contains the 3(1)-phenyltriazole ring, is related to phenanthrenequinone, the reduction potential of X would be 0.055 v. higher than that of anthraquinone, or 0.210 v.; but the actual value, 0.256 v., is appreciably higher than this. The two imidazole derivatives, V and XII, may be compared in the same way, though they are not isomeric. Since the potential of the angular substance, V, is 0.070 v. above that of phenanthrenequinone, it would be expected that the value for the linear

isomer, β,β -naphthimidazolequinone, would be in the neighborhood of 0.225 v. The potential of the N-methyl-N-phenyl derivative (XII) of this compound should be even lower than this value and, since the actual value is 0.320 v., it seems clear that the assumption that the heterocyclic ring bears the same relationship to the benzene ring in the linear tricyclic compounds as in the angular series does not hold. There seems to be some specific property of the benzenoid and of the heterocyclic rings which only becomes manifest in the linear tricyclic series.

Now the potential of anthraquinone itself is much lower than can be accounted for by supposing that the effect of two phenylene groups attached to *p*-benzoquinone is just twice the effect of one. It is difficult to account for this fact on the basis of the structure of anthraquinone, but it must be remembered that the reduction potential of a quinone is a measure of the free energy of the conversion of the quinone into its hydroquinone and that the structure of the reduction product must also be taken into consideration. The abnormally low potential of anthraquinone may not be due to any peculiarity of the quinone but to some specific property of anthrahydroquinone which renders it particularly reactive and prone to pass over into its oxidation product. It does not appear unwarrantable to consider that this property is due to an ortho-quinonoid structure of the hydroquinone, according to Formula XIII,

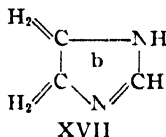
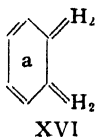


in which Ring a, like the corresponding ring of *o*-benzoquinone, has a tendency to pass into the truly benzenoid condition and so contributes to the reactivity of the molecule as a whole.

If the Armstrong formulation of anthracene is adopted for heterocyclic analogs of this hydrocarbon, the question arises as to whether Ring a or Ring a' of XIII has been replaced by the heterocycle, that is, whether it is the benzene ring or the heterocycle which has the quinonoid structure. The problem is similar to the question of the structure of unsymmetrical azines which was explored by Kehrman²⁰ and may, in theory, be treated in the same way. If, for example, the ring XIV-a is more reactive than XV-b, the compound will exist chiefly in the form of XV; this form would predominate in the equilibrium mixture. Any nucleus which has the *o*-quinonoid grouping of linkages possesses a certain tendency to rearrange into a more stable structure, but the rearrangement

²⁰ Kehrman, *Ber*, 31, 977 (1898)

of XIV into XV, which would result if the strained *o*-quinonoid condition of XIV-a is to be relieved, is opposed by the reverse rearrangement due to the tendency of XV-b to pass into a condition of greater stability. Thus an equilibrium between the two forms would result and the point of this equilibrium would depend upon the relative reactivities, in the sense indicated, of the quinonoid rings XIV-a and XV-b. Various methods of estimating these reactivities are conceivable, and one of them is being investigated by Fries.²⁶ He states that dihydro-imidazole (XVII) is a



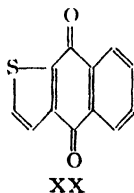
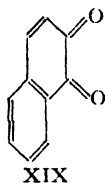
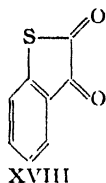
stable substance which is devoid of the tendency to pass into dehydrogenated derivatives which characterizes dihydrobenzene (XVI). Since these two compounds have structures similar to XIV-a and XV-b, it is reasonable to suppose that XV-b is the least reactive of the two and, therefore, that the substance in question corresponds to XV. The substance thus differs from anthrahydroquinone or any other heterocyclic analog in a very essential respect and a simple relationship between these various compounds is not to be expected. From the foregoing analysis we can only say that the linear arrangement of the three nuclei should not result in such a pronounced tendency to undergo oxidation in the case of the heterocyclic substance, XV, as in the case of anthrahydroquinone, in other words, the reduction potential of the quinone corresponding to XV should be higher than that of anthraquinone and higher by an amount not accounted for by the relationship between corresponding angular tricyclic compounds. It is clear that this interpretation agrees with the experimental results.

In the case of the triazole derivative, X, the results indicate that the triazole nucleus approximates much more closely the character of the benzene nucleus. The few pertinent chemical facts which are known²⁶ concerning the triazoles support this conception.

It thus appears highly probable that the specific factor which is operative only in the linear tricyclic series is concerned with the *o*-quinonoid structure of anthracene and its analogs. In order to test this hypothesis further, it is necessary to have some general method of determining the relative tendency of the various cyclic systems to rearrange from the quinonoid into the benzenoid condition. It occurred to us that very precise information on the point in question would be furnished by the determination of the reduction potentials of heterocyclic analogs of *o*-benzoquinone or its derivatives in the event that such determinations

²⁶ Fries, *Ann.*, 454, 127 (1927).

are possible. At present, however, very few quinones of the type indicated are known. We have studied one such compound, thionaphthenequinone (XVIII), and have found that it can be brought within the scope of the



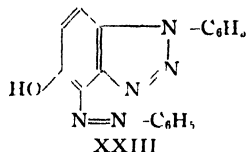
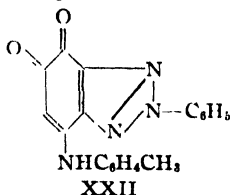
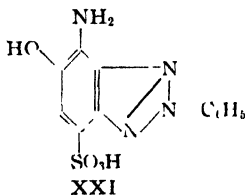
electrochemical method of treatment. Its reduction potential ($E_0 = 0.264$ v.) is very low in comparison to that of β -naphthoquinone, XIX ($E_0 = 0.597$ v.). This means that the thiophene ring, present in the reduction product of XVIII, is much more prone to pass into the quinonoid or dihydride condition than is benzene. It is a less stable system.

The relatively high potential of thiophanthrenequinone XX (E_0 , 0.250 v., as compared with 0.155 v. for anthraquinone) may well be related to this fact, though data on other thiophene derivatives are required before the question can be properly analyzed.

Experimental Part

1. **Synthesis of 2-Phenylbenzotriazole-4,5-quinone-7-sulfonic Acid (II).**—2-Phenyl-4-nitroso-5-hydroxybenzotriazole, a compound which has been described by Fries and Roth,^{24b} formed the starting point for this synthesis. In preparing this substance, 2-phenyl-5-aminobenzotriazole was obtained in 76% yield by reduction of the corresponding nitro compound with stannous chloride,²⁷ and converted into the hydroxy derivative in the manner described by Fries and Roth, though it was found that the use of boric acid¹ improved the latter process considerably. By the addition of 1.5 molecular equivalents of boric acid to the solution of the diazotized amine before boiling the mixture, the yield was increased from 60% to 85–90% and the time required for the complete evolution of nitrogen was greatly shortened.

2-Phenyl-4-amino-5-hydroxybenzotriazole-7-sulfonic Acid (XXI).—The 4-nitroso derivative prepared from 2.1 g. of 2-phenyl-5-hydroxybenzotriazole was suspended, while still moist, in a solution of 3.1 g. of sodium bisulfite in 150 cc. of water and the



mixture was stirred for several hours until no more material appeared to go into solution. The solution was then filtered, concd. hydrochloric acid was added in excess, and the solution was allowed to stand at 35° for one day, when the separation of almost colorless crystals of the reaction product had ceased. The substance is very sparingly soluble in

²⁷ Kehrman and Messinger, *Ber.*, **25**, 898 (1892). Willgeroth, *J. prakt. Chem.*, [2] **46**, 131 (1892).

water. It dissolves readily in hot sodium bisulfite solution, and on cooling the solution deposits yellow needles of the sodium salt. The free acid was obtained in pure condition, in the form of colorless micro-crystals, from the crystallized sodium salt. It retains combined water even on drying in a vacuum at 100°.¹⁸

Anal. Calcd. for $C_{12}H_{10}O_4N_4S \cdot 1\frac{1}{2}H_2O$: C, 43.23; H, 3.93. Found: C, 43.13; H, 3.88.

Potassium 2-Phenylbenzotriazole-4,5-quinone-7-sulfonate (II).—Oxidation of the above compound was accomplished by stirring 1 g. of the material into 2 cc. of 25% nitric acid. On warming slightly all of the material dissolved and orange needles of the ammonium salt of the quinone soon began to separate. After adding saturated ammonium chloride solution and cooling, the precipitate was collected and well washed with ammonium chloride solution. The salt dissolves readily in water and is moderately soluble in alcohol. The potassium salt, which is less soluble, crystallized from water in the form of small, orange-yellow needles.

Anal. Calcd. for $C_{12}H_8O_4N_4SK$: K, 11.39. Found: K, 11.35.

This quinone is very similar in properties to 1,2-naphthoquinone-4-sulfonic acid. It is decomposed by alkalis, giving a green solution from which a red substance precipitates on acidification, while on treatment with concd. sulfuric acid, sulfur dioxide is rapidly evolved and a yellow substance is precipitated on diluting the red, acid solution. The compound is readily reduced by sulfur dioxide and can be condensed with amines. For the purpose of characterization, the *p*-toluidino compound was prepared.

2-Phenyl-7-(*p*-toluidino)-benzotriazole-4,5-quinone (XXII).—A mixture of aqueous solutions of equivalent weights of ammonium 2-phenylbenzotriazole-4,5-quinone-7-sulfonate and *p*-toluidine was heated at the boiling point for ten minutes. The toluidino compound, which was deposited in the form of small, dark red needles, was crystallized from methyl alcohol, in which it is moderately soluble; m. p., 215°.

Anal. Calcd. for $C_{19}H_{14}O_4N_4$: C, 69.07; H, 4.27. Found: C, 69.02; H, 4.42.

2. Experiments in the 1-Phenylbenzotriazole Series.—1-Phenylbenzotriazole-4,5-quinone (I) was prepared by the method of Fries and Empson² and crystallized from glacial acetic acid. In addition to the properties reported by these authors, it was noted that, although the quinone is readily reduced by sodium hyposulfite, it is completely insoluble in bisulfite solution. It was also found that nitrous acid is without action on 1-phenyl-5-hydroxybenzotriazole, though this compound couples with diazotized amines.

1-Phenyl-4-benzene-azo-5-hydroxybenzotriazole (XXIII).—To a solution of 2.1 g. of 1-phenyl-5-hydroxybenzotriazole² in 25 cc. of water containing 2 g. of sodium hydroxide was added a benzene diazonium chloride solution prepared from 0.93 g. of aniline. After warming for a time and neutralizing the solution, the product was collected and crystallized from alcohol; yield, 2.7 g. (85%). It forms bright red crystals which are sparingly soluble in organic solvents and soluble in alkalis.

Anal. Calcd. for $C_{18}H_{13}ON_4$: C, 68.66; H, 4.16. Found: C, 68.49; H, 4.29.

Attempts to reduce the azo compound to an amine with sodium hyposulfite in alkaline solution were unsuccessful; reduction took place but no product was obtained corresponding in properties to the substance desired.

3. α,β -Naphthotriazole-4,5-quinone.—In preparing this compound according to the directions of Zincke and Noack⁷ it was found that β -naphthoquinone, which forms the starting-point of the synthesis, could be most satisfactorily nitrated in the following

¹⁸ Compare the behavior of 1-amino-2-naphthol-4-sulfonic acid, Schmidt, *J. prakt. Chem.*, [2] 44, 523 (1891).

ether and the ether evaporated. A brown oil remained. When this was dissolved in alcohol and poured into water, an emulsion was formed and crystallization finally took place. These crystals were purified from dilute alcohol.

The diacyls were saponified by dissolving in 10% potassium hydroxide and then acidifying with hydrochloric acid. The precipitate was purified by recrystallization from dilute alcohol. All analyses were made by the Kjeldahl method.

Summary

1. The heavier *iso*-carbopentoxy group replaces both the *n*- and the *isocarbobutoxy* from the nitrogen in diacyl derivatives of *o*-aminophenol.

2. The benzoyl group does not behave the same with the *n*-carbopropoxy and the *iso*-carbopropoxy groups in diacyl derivatives of *o*-aminophenol. In the case of the *n*-carbopropoxy derivative the benzoyl group goes to the nitrogen, but in the case of the *isocarbopropoxy* group the benzoyl group goes to oxygen.

3. New diacyl derivatives of *o*-aminophenol have been prepared and studied.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HYDROGEN-ETHYLENE REACTION IN THE PRESENCE OF EXCITED MERCURY ATOMS

BY A. R. OLSON AND CHARLES H. MEYERS

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In a former paper the authors¹ concluded from semi-quantitative evidence that ethane was formed from hydrogen and ethylene when a mixture of the latter is illuminated with ultraviolet light in the presence of mercury vapor. However, it was also known at this time that in addition to ethane other substances must be formed. The experiments about to be described were undertaken to determine the products of the reaction more definitely.

The experimental arrangement used to expose the gas to the light was the same as that described in our former paper except that the gases were kept in constant circulation.

The ethylene and hydrogen were prepared as described in our former paper. Ethane was prepared by treating an ether solution of C_2H_5MgI with dilute sulfuric acid. The ethane was dried and purified by bubbling through concentrated sulfuric acid and by means of liquid air fractionally distilled three times, the middle portion only being saved for each subsequent distillation.

In Experiment I a mixture of hydrogen at a pressure of 39 cm. and ethyl-

¹ Olson and Meyers, *THIS JOURNAL*, **48**, 389 (1926).

manner, the success of the process depending largely on having the proper acid concentration. Twenty g. of β -naphthoquinone was stirred into 40 cc. of nitric acid (sp. gr. 1.40) and the mixture was warmed on the water-bath until nitric oxide became apparent and the quinone went into solution (about one minute). The flask was at once transferred to an ice-bath and several small pieces of ice were added. On stirring, crystallization took place almost immediately and after 15 minutes the product was collected and washed successively with concd. nitric acid, glacial acetic acid and ether; yield, 20.6 g. (80%); m. p., 156° . Conversion of this compound, through its hydroquinone, into 3-amino-1,2-naphthohydroquinone was accomplished in 85% yield. We have nothing to add to Zincke and Noack's description of the remaining steps or of the triazole quinone except that this substance, like most *o*-quinones, dissolves readily in sodium bisulfite solution. On adding acid to such a solution, the quinone is apparently reduced by sulfur dioxide, for a salt of the hydroquinone is slowly precipitated.

α,β -Naphthotriazolequinone was also obtained by the oxidation of α,β -naphthotriazole²⁸ with chromic anhydride in glacial acetic acid solution. Samples prepared in these two ways were purified by crystallization from glacial acetic acid solution and compared by determination of the reduction potential, since the substance has no melting point. The two samples were identical.

4. α,β -Naphthimidazole-4,5-quinone (V).—A mixture of 1 g. of 1,2-diamino-3,4-dihydroxynaphthalene dihydrochloride⁷ and 1.1 g. of fused sodium acetate was covered with 85% formic acid and heated under the reflux for one hour. The excess acid was then removed by distillation and the residue dissolved in water. After filtering, the solution was neutralized with ammonia and allowed to stand until separation of the naphthimidazolehydroquinone was complete. The substance was colored bluish-gray due to oxidation; it was not isolated but was at once converted into the quinone by adding it to sufficient nitric acid (sp. gr. 1.4) to bring the material into solution. The orange quinone precipitated on the addition of a small amount of water. When crystallized from alcohol, it formed clusters of orange needles which darken at 210° but remain unmelted at 250° . It is insoluble in benzene or toluene and moderately soluble in alcohol or glacial acetic acid. The solution in concd. sulfuric acid is a deep orange-red; the alkaline solution is rose color. The quinone is readily reduced by sodium hyposulfite and, when the solution in sodium bisulfite is acidified, a salt of the hydroquinone separates.

Anal. Calcd. for $C_{11}H_6N_2O_2$: C, 66.66; H, 3.05. Found: C, 66.50, H, 3.17.

5. *E.m.f. Measurements.*—The results given in Table I were obtained by measuring the potential difference between a half-cell containing the quinone-hydroquinone solution and a hydrogen electrode half-cell containing the same solvent. The potentiometer was accurate to 0.5 mv. Titanous chloride solutions, containing approximately from 0.03 to 0.4% of this reagent, were prepared from the 20% standardized solution immediately before each determination. In those cases in which the solubility of the quinone is very slight, the solution was prepared by digesting an excess of the quinone with 300 cc. of the solvent at 60° , cooling to 20° and filtering. Judging from the solubility of phenanthrenequinone in water, which is 3.6×10^{-3} at 25° ,³⁰ the solutions of the quinones ranged in molar concentration from about this value to about 1×10^{-3} . The concentration of titanous chloride required to furnish a titration curve of suitable dimensions was determined in a preliminary experiment.

Most of the measurements require little comment, though it may be noted that with all of the compounds, with the exception of the first one listed in Table I, constant

²⁸ Diels, *Ber.*, **54**, 226 (1921).

³⁰ Knox and Will, *J. Chem. Soc.*, 115, 850 (1919).

ene at a pressure of 25 cm. in the presence of mercury vapor was illuminated by ultraviolet light for thirty-nine hours, at which time the pressure drop was 24 cm. At the end of this time further illumination did not cause a further pressure decrease.

In Experiment II a mixture of hydrogen at a pressure of 40 cm. and ethylene at 2 cm. in the presence of mercury vapor was illuminated until the pressure became constant at 40 cm.

In Experiment III ethane at a pressure of 66 cm. and mercury vapor were exposed to ultraviolet light for fifty hours, at the end of which time the pressure drop was less than 2%.

In a fourth experiment pure unilluminated ethane was used.

The mixtures in these four experiments were then analyzed in the positive-ray apparatus described by Hogness and Lunn.² By this method the gases are ionized by electronic impact and the ions are then sent through electric and magnetic fields. It is possible to plot the number of ions of a given mass against the mass. Due to the characteristics of the apparatus, ions of a definite mass are distributed about the point corresponding to the mass of the ion, so that it is necessary to use the area under the curve as a measure of the number of ions rather than the height of the peak. This measure of the number of ions assumes that the efficiency of ionization by electronic impact of the various molecular species is the same. In the case which we are about to consider this condition is probably closely obeyed. The results of these positive-ray analyses are summarized in Table I, where the amount of ethane, for convenience, is taken as unity.

TABLE I
RESULTS OF POSITIVE-RAY ANALYSES

Expt. no.	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
I	0.018	1	0.64	0.42
II	0.22	1	0.04	0.0008
III	0	1	0	0
IV	0	1	0	0
Ratio I/II	0.082	1	16	525

Experiments III and IV show that under these conditions ethane undergoes no reaction large enough to be detected.

From the total amount of ethylene used and the relative amounts of

TABLE II
FINAL PRESSURES IN CM. OF MERCURY

Expt. no.	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	H ₂	C ₂ H ₄
I	0.16	8.9	5.8	3.75	21	0
II	0.376	1.71	0.068	0.0013	38	0
Ratio I/II	0.425	5.2	85	2880		

² Hogness and Lunn, *Phys. Rev.*, **26**, 44 (1925).

potentials were reached only after considerable periods of time, and a complete titration often required three or four hours. In the case of the 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid, electrode equilibrium was established with great rapidity in aqueous solution, but the measurements in alcoholic solution were unsatisfactory because of the decomposition of the quinone. The first few points of the titration curve, instead of forming the usual inflection, fell on a straight line which included the point corresponding to the potential of the solution before any reducing agent had been added. This is clear evidence of the reaction of the quinone and the solvent with the production of reduction products and this conclusion is supported by the fact that the potential at half-reduction was not reproducible and was much lower than the value which might reasonably be predicted for the normal potential. Titration curves of exactly similar characteristics were obtained with 1-phenylbenzotriazole-4,5-quinone (I) and the results were consequently rejected.

A curious behavior was observed in carrying out measurements with 1-phenyl- β,β -naphthotriazole-4,9-quinone (X). On adding an increment of titanous chloride solution, the e.m.f. of the cell very slowly changed to a less positive value and finally became constant. When the quinone had been about half reduced, equilibrium was established much more rapidly, but somewhat beyond this point the cell potential fell in the normal manner after the addition of the reducing agent, remained poised at a constant value for a few minutes, and then began to rise. The effect was particularly evident toward the final stages of reduction. This behavior may be due to the action of the reducing agent on parts of the molecule other than the quinone grouping. By carrying out rapid titration in which the "poised potentials" were recorded, values for the normal potential were obtained which are probably not greatly in error, though the slopes of the titration curves, indicated by ΔE , deviated widely from the theoretical. In the case of the *p*-tolyltriazole derivative XI the situation was similar, though the potentials did not rise as rapidly as before and the results are somewhat more accurate.

Since thionaphthenequinone is the first substance of its type which has been found to give, in mixtures containing its reduction product, definite electrode potentials which conform to the usual electrochemical equation, it seems advisable to include further details concerning our experiments with this compound than are given in Table I. The results of a typical titration, together with the values for the normal potential which have been calculated from the equation $E_0 = E_{\text{cell}} - 0.0296 \log [\text{Oxid.}]/[\text{Red.}]$, are given in Table II. The oxidation-reduction half-cell

TABLE II

TITRATION OF THIONAPHTHENEQUINONE IN 0.1 *N* HCL SOLUTION WITH TiCl_3 . END POINT = 8.70 CC. E_0 BY GRAPHICAL INTERPOLATION = 0.2635 v.

TiCl_3 , cc.	E_{cell} , v.	E_0 (calcd.), v.	TiCl_3 , cc.	E_{cell} , v.	E_0 (calcd.), v.
0.0	(0.571)	...	4.0	0.2655	0.2634
.5	.314	(0.278)	4.5	.2625	.2634
1.0	.294	(.268)	5.0	.2955	.2633
1.5	.2850	.2648	6.0	.2528	.2631
2.0	.2790	.2635	7.0	.2440	.2622
2.5	.2745	.2628	8.0	.226	(.277)
3.0	.2716	.2634	8.5	.196	(.244)
3.5	.2683	.2639	8.7	.125	...

Av. = 0.2634 v.

substances formed, we can calculate the final pressures in cm. of mercury of all the gases. The results of these calculations are collected in Table II.

From the experiments already reported in our former paper, as well as from the results of other investigators, it is shown that at least two primary processes occur



where Hg^* stands for the excited state, and

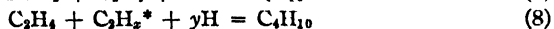
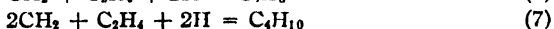


In the present set of experiments the formation of methane and propane demonstrate that a third primary process occurs by the breaking of the ethylene bond



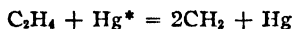
It seems reasonable to assume that the amount of CH_2 formed is proportional to the amount of ethylene present.

We must now consider the reactions between the products of these primary reactions and the original substances to form the final products. It is clear at the outset that the chance of CH_2 adding molecular hydrogen must be very low, for otherwise the concentration of methane would be much higher or the concentration of propane much lower than was found. There remain, then, the following reactions to be considered



where C_2H_2^* is a molecule of ethylene which has been activated probably by loss of hydrogen.

From the postulated reactions and the final pressures of the products, we can calculate the amount of ethylene (measured in cm. of mercury) of the reaction



which is required to produce the calculated amounts of the above products. The results of these calculations are collected in Table III.

TABLE III
CALCULATED AMOUNTS OF ETHYLENE (CM. OF MERCURY)

Expt. no.	By reactions (5), (6) and (7)	By reactions (5), (6) and (8)
I	6.74	2.99
II	0.222	0.222
Ratio I/II	30.4	13.5

We have already assumed the amount of CH_2 formed to be proportional to the ethylene pressure, or 12.5 times as much in Experiment I as in

contained a gold-plated and a platinized platinum electrode, both of which were always used in making the readings. While with most compounds the two readings usually agree well, it was found that with thionaphthenequinone the gold-plated electrode easily became polarized and that the potentials recorded were inconstant, irreproducible and differed from those recorded on the platinized electrode, which behaved in normal fashion, by 2-10 mv. These readings were disregarded. No consistent results were obtained with either type of electrode in alcoholic solution.

We wish to acknowledge our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant used to purchase the electrical instruments employed in this work.

Summary

1. On comparing the reduction potentials of the quinones of the naphthalene and phenanthrene series with quinones containing the 2-phenyltriazole nucleus in place of one of the benzene rings, it has been found that a striking similarity exists between this heterocyclic nucleus and benzene. The 1,2,3-triazole ring is similar to these other two and probably has the structure of the 2-phenyl derivative, for a quinone containing the 3-phenyltriazole grouping is much higher in potential than the corresponding triazolequinone or its 2-phenyl derivative.

2. Preliminary results indicate that the pyridine and the imidazole nuclei do not produce a lowering in the potential of quinones to which they are attached which is at all comparable with the effect of a phenylene group.

3. Heterocyclic analogs of anthraquinone do not bear the same relation to this substance which the angular isomers bear to phenanthrenequinone. A tentative explanation of these facts, based upon the *o*-quinonoid theory of the structure of anthracene, has been suggested.

4. The reduction potential of thionaphthenequinone, the first substance of its type to which the electrochemical method has been successfully applied, has been determined in aqueous solution.

BRYN MAWR, PENNSYLVANIA

Experiment II. If we compare this ratio with the required amount of CH_2 in Table III, we see that it agrees very closely if we assume mechanisms (5), (6) and (8), but it is less than half of that required for mechanisms (5), (6) and (7). We conclude, therefore, that Reaction (7) does not take place to an appreciable extent under these conditions. The tremendous decrease of butane with decrease of ethylene must be accounted for by an increased rate of hydrogenation of the activated ethylene molecules.

The fact that Reaction (7) does not take place is in agreement with the fact that the higher hydrocarbons are absent, for these would all involve reactions between three or more ethylene molecules or radicals formed from ethylene before complete hydrogenation took place.

At high pressures of ethylene, the chance of reaction between CH_2 and ethylene is large compared with the chance of CH_2 being completely hydrogenated, whereas at low pressures of ethylene almost all of the CH_2 is removed as methane. This is clearly shown by reference to Table I. The average pressure of ethylene in Experiment I is 12.5 times as high as in Experiment II. The amount of methane formed in Experiment II per unit amount of ethane is 12.2 times as high as that found in Experiment I, while the amount of propane decreases at the same time 16-fold.

We take pleasure in acknowledging our indebtedness to Mr. Hamline M. Kvalnes of this Laboratory for making the positive-ray analyses.

Summary

Mixtures of hydrogen and ethylene react when subjected to the action of excited mercury atoms. By positive-ray analysis it is shown that the products of reaction are methane, ethane, propane and butane. Mechanisms for the formation of these substances are proposed. It is demonstrated that the carbon-hydrogen bond in ethylene and the ethylene bond itself require less than 4.9 volts of energy for rupture.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 19]

UNSYMMETRICAL PHENANTHRIDONES. II. A NEW PREPARATIVE METHOD: 7-NITROPHENANTHRIDONE BY BECKMANN REARRANGEMENT OF 2-NITROFLUORENONE OXIME

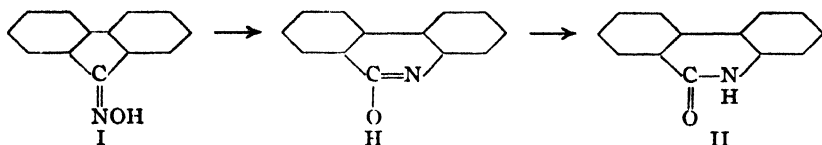
BY F. J. MOORE AND E. H. HUNTRESS¹

RECEIVED AUGUST 1, 1927

PUBLISHED OCTOBER 5, 1927

Shortly after the discovery of the Beckmann rearrangement of oximes in 1884, Beckmann and Wegerhoff² attempted to expand the scope of the new reaction to the oximes of cyclic ketones. Studying fluorenone oxime as a typical example, they reported that heating with a mixture of acetic anhydride and hydrogen chloride in a closed tube effected only acetylation, and that the use of concentrated sulfuric acid as a rearranging agent yielded a mixture of sulfonic acids. After boiling the oxime with a solution of phosphorus pentachloride in phosphorus oxychloride, however, removal of the solvent left a viscous oil from which they were unable to isolate a chloride. Nevertheless, after treatment with water, the oil yielded a yellow powder from which a nearly colorless, chlorine-free compound melting at 287° was obtained. This material was formed in such small amount and proved so difficult to purify that after an analysis its definite characterization was abandoned.

Application of the usual principles of Beckmann rearrangement to the case of fluorenone oxime (I) indicates that the rearrangement product should have been phenanthridone (II).



At the time of Beckmann and Wegerhoff's work this substance was unknown, and although only four years later Graebe and Wander³ prepared the material by a method which demonstrated its structure, and their melting point of 293° was very close to that of Beckmann's product, no attempt to establish the identity of the two substances has ever been reported.

¹ This paper is constructed from a second portion of the thesis submitted by E. H. Huntress to the Faculty of the Massachusetts Institute of Technology, in January, 1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Owing to the death of Professor Moore, the junior author assumes responsibility for the statements in this article.

² Beckmann and Wegerhoff, *Ann.*, **252**, 35 (1889).

³ Graebe and Wander, *Ann.*, **276**, 245 (1893).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
No. 558]

RESEARCHES ON THIAZOLES. XIV. THE SYNTHESIS OF 2-ORTHO- AND META-AMINOPHENYL-6-METHYLBENZOTHAZOLES; NEW ISOMERS OF DEHYDROTHIO-PARATOLUIDINE, AND OF INCIDENTAL COMPOUNDS¹

BY MARSTON TAYLOR BOGERT AND LEONARD SMIDTH²

RECEIVED AUGUST 2, 1927

PUBLISHED DECEMBER 10, 1927

In recent papers by Bogert and Allen,^{3,4} there have been described isomers of the well-known dye intermediate dehydrothio-*p*-toluidine carrying the methyl group in Positions 5 or 7, and the amino groups in various positions on the 2-phenyl nucleus. The present contribution supplements this by reporting additional isomers in which the methyl, but not the amino, group is located as in dehydrothio-*p*-toluidine itself.

These new isomers were synthesized in the same way as outlined in previous papers from these Laboratories dealing with other isomers, namely, by condensing the zinc salt of the appropriate aminothiocresol with *o*- or *m*-nitrobenzoyl chloride to the 2-nitrophenyl-6-methylbenzothiazole and then reducing the latter to the amine.

These amines should yield dyes corresponding to Chloramine Yellow (Colour Index No. 814), when their sodium sulfonates are oxidized by alkaline hypochlorite solution. This reaction followed a normal course with the *m*-aminophenyl derivative, giving a product of similar properties to Chloramine Yellow, which dyed cotton a much paler shade and was manifestly inferior to it. In the case of the *o*-aminophenyl derivative on the other hand, the reaction pursued an abnormal course and no Chloramine Yellow dye was obtained.

Experimental Part

2-(*m*-Nitrophenyl)-6-methylbenzothiazole.—An intimate mixture of 3 g. of zinc 2-amino-5-methylphenyl mercaptide with 3.7 g. of *m*-nitrobenzoyl chloride was heated at 100° for an hour while the viscous melt was well stirred. The pulverized cold fusion cake was warmed for an hour with *N* sodium hydroxide solution and the undissolved material then removed, washed, dried and crystallized from glacial acetic acid. Small yellow needles were obtained, m. p. 166° (corr.), readily soluble in chloroform, moderately soluble in boiling alcohol and practically insoluble in ether, acetone or benzene; yield, 1.4 g. or 58%.

Anal. Calcd. for $C_{14}H_{10}O_2N_2S$: C, 62.22; H, 3.70. Found: C, 62.09; H, 4.02.

2-(*m*-Aminophenyl)-6-methylbenzothiazole.—A mixture of 1.5 g. of the above nitro derivative, 5 cc. of concd. hydrochloric acid, 95 cc. of water and 10 g. of granulated

¹ Presented in abstract before the Division of Dye Chemistry at the Baltimore Meeting of the American Chemical Society, April 8, 1925.

² DuPont Fellow at Columbia University for the academic year 1923-24.

³ Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926).

⁴ Bogert and Allen, *This Journal*, **49**, 1315 (1927).

That it is not unreasonable to expect Beckmann rearrangement of fluorenone oxime is indicated by the studies of Wallach⁴ who showed that cyclomethylene ketoximes were quite generally rearranged by concentrated sulfuric acid to isoximes or lactams of amino acids, into which they could readily be converted by hydrolysis. Thus, cyclopentanone oxime yielded the six-membered piperidone, otherwise known as the lactam of δ -aminovaleric acid. Again, Beckmann and Liesche,⁵ in an article which appeared during the progress of this research, have effected a normal rearrangement both of quinone monoxime and of anthraquinone monoxime. Except for Beckmann's early work, however, the only reference to the possible rearrangement of fluorenone oxime itself is the report of Pictet and Gonset⁶ who found that when heated with zinc chloride at 260–280°, a 30% yield of phenanthridone identical with Graebe and Wander's product could be isolated. Although the conditions used by Pictet and Gonset were far more vigorous than those of an ordinary Beckmann transformation, their results strengthened our belief that Beckmann and Wegerhoff's reaction product was really phenanthridone.

Our interest in this reaction was based upon the hope of using the Beckmann rearrangement of substituted fluorenone oximes as a method for the preparation of substituted phenanthridones. Not only is the literature of these substances very fragmentary but the synthesis of certain monosubstitution products from the corresponding diphenic acid derivatives is a process of considerable length and difficulty.⁷

We have repeated Beckmann and Wegerhoff's experiments on the rearrangement of fluorenone oxime by phosphorus pentachloride and by the method of mixed melting points established the identity of the product with phenanthridone synthesized according to Graebe and Wander.³ The change apparently involves nearly quantitative conversion of the oxime to a chloride which hydrolyzes slowly or rapidly, according to conditions, to give excellent yields of phenanthridone. Since our purpose was merely to establish the validity of the rearrangement, we have not attempted to study its mechanism in detail.

Although fluorenone oxime itself can exist in but one form, theory predicts for each of the unsymmetrical monosubstitution products the possible existence of two stereo-isomers, according to whether the substituted nucleus is on the same or opposite side of the carbon-nitrogen double bond as the oxime hydroxyl group. Beckmann rearrangement of these isomers would be expected to yield two different but isomeric

⁴ Wallach, *Ann.*, **309**, 1 (1899); *Ann.*, **312**, 171 (1900); *Ann.*, **346**, 249 (1906).

⁵ Beckmann and Liesche, *Ber.*, **56**, 1 (1923).

⁶ Pictet and Gonset, *Arch. sci. phys. nat.*, [4] **3**, 3751 (1897); *Chem. Centr.*, **1897**, I, 413.

⁷ Moore and Huntress, *THIS JOURNAL*, **49**, 1324 (1927).

tin was boiled for two hours, although a clear solution resulted after one hour's boiling. The acid solution was made strongly alkaline with 4 *N* sodium hydroxide solution and kept warm for an hour. The insoluble material, when removed and crystallized from alcohol, formed colorless needles, m. p. 181° (corr.), easily soluble, without appreciable fluorescence, in alcohol, acetone, ether, chloroform or benzene; yield, 0.85 g. or 64%.

Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 70.00; H, 5.00. Found: C, 70.29; H, 5.14.

Sulfonation of 2-(*m*-Aminophenyl)-6-methylbenzothiazole.—A solution of 0.75 g. of the thiazole in 5 cc. of concd. sulfuric acid was cooled to 25° and 5 cc. of fuming (50% free SO_3) sulfuric acid added gradually while the temperature of the solution was maintained below 50°. After the solution had been kept at 40–50° for eight hours, it was entirely soluble in dilute ammonium hydroxide solution and the sulfonation was adjudged complete. It was poured upon cracked ice, the yellow flocculent precipitate collected, dissolved in warm dil. caustic alkali, the alkaline solution reprecipitated with sulfuric acid and the precipitate dried in the oven. The product was a dark brown solid; yield, 0.7 g.

A Yellow Dye Analogous to Chloramine Yellow.—A solution of 0.5 g. of the above sulfo acid in 100 cc. of water and 0.1 g. of sodium hydroxide, when oxidized at 10–15° by an aqueous solution of sodium hypochlorite, turned violet at first, then wine-red and cloudy. After it had stood for twenty-four hours, dil. sulfuric acid was added and the precipitate removed and dried. It formed a brown powder which gave a deep carmine-red color with concd. sulfuric acid, similar to that produced from Chloramine Yellow itself.

Comparative dyeing tests (2%) on cotton showed that the shades obtained were paler than those yielded by Chloramine Yellow, but that in other respects it resembled the latter closely.

2-(*o*-Nitrophenyl)-6-methylbenzothiazole.—When a mixture of dry *o*-nitrobenzoyl chloride and the zinc mercaptide was warmed, a reaction ensued with explosive violence and carbonization. When the chloride (2 cc.) and mercaptide (2 g.) were dissolved in glacial acetic acid (5 cc.), no reaction was perceived in the cold, so the solution was heated at 100° for thirty minutes, then poured into water and the precipitate collected and warmed for an hour with *N* sodium hydroxide solution, which changed it to a viscous tar from which no crystalline product could be obtained. It was therefore distilled under diminished pressure and a product secured which congealed to a yellow gum; yield, 0.9 g. or 57%. As this product looked like unpromising material for analysis, it was reduced (1 g.) directly to:

2-(*o*-Aminophenyl)-6-methyl-benzothiazole, by boiling it for three hours with concd. hydrochloric acid (10 cc.), water (90 cc.) and granulated tin (10 g.). The double salt formed remained insoluble in the acid solution and was removed and digested with warm caustic soda. The crude, insoluble amine was crystallized from alcohol and then appeared in rosetts of colorless needles, m. p. 137° (corr.); yield, 0.7 g. or 62%. The compound dissolved freely in alcohol, acetone, chloroform, carbon tetrachloride, ether, carbon disulfide or benzene. The solution in alcohol or acetone exhibited a fine blue fluorescence.

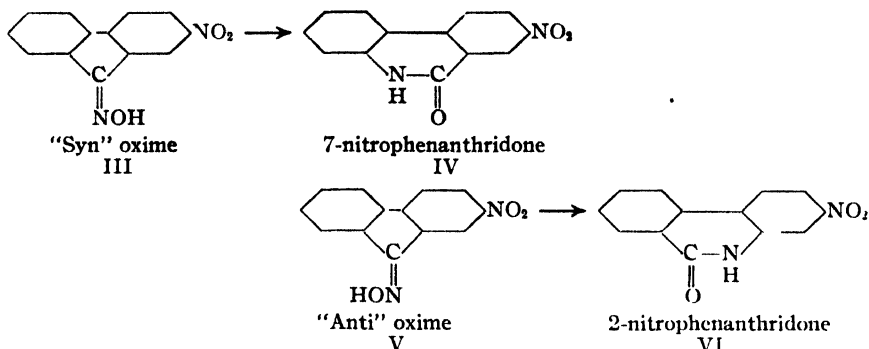
Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 70.00; H, 5.00. Found: C, 69.90; H, 5.12.

The Acetyl Derivative, from the amine and acetic anhydride, crystallized from alcohol in colorless needles, m. p. 150° (corr.), easily soluble in alcohol, ether or benzene; yield, 77%.

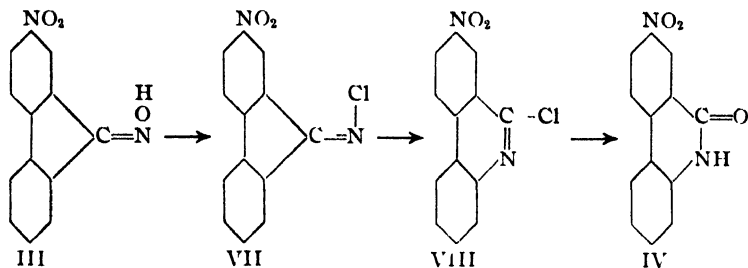
Anal. Calcd. for $C_{16}H_{14}ON_2S$: C, 68.08; H, 4.96. Found: C, 67.64; H, 4.87.

The sulfonation of the *o*-aminophenyltoluthiazole (1 g.) was attempted with fuming sulfuric acid, by the process outlined for the *m*-isomer. The sulfonation solution when

substituted phenanthridones. Thus, assuming with Meisenheimer^{8,9,10} that *trans* interchange of radicals occurs, the expected products from the two forms of 2-nitrofluorenone oxime would be as follows



We have found, however, that treatment of 2-nitrofluorenone with hydroxylamine hydrochloride gives 75–85% yields of one of the two possible stereo-isomers, and that this product is rearranged by phosphorus pentachloride and oxychloride to give almost quantitative yields of 7-nitrophenanthridone. We have shown that the direct effect of the phosphorus halides is to replace chlorine for hydroxyl but that a mixture of two compounds is obtained which analyzes correctly for chlorine content yet is not readily separable by crystallization. Since reaction of this mixture with water yields 87% of 7-nitrophenanthridone with no indication of any of the 2-nitro isomer, we suspect that the mixture of chlorides represents an equilibrium between the oxime chloride and its rearrangement product, and that hydrolysis of the latter causes progressive conversion to the single 7-nitrophenanthridone as follows.



Whether this suspicion be confirmed or not, it is certain that oximation of 2-nitrofluorenone gives excellent yields of one stereo-isomer which undergoes smooth Beckmann transformation to give 7-nitrophenanthridone in yield of 90%. The process is therefore admirably suited to

⁸ Meisenheimer, *Ber.*, **54**, 3206 (1921).

⁹ Meisenheimer and Meis, *Ber.*, **57**, 289 (1924).

¹⁰ Meisenheimer, Zimmermann and Kummer, *Ann.*, **446**, 205 (1926).

poured upon ice gave a dark green, gelatinous precipitate which dried out in the oven to a hard, black solid; yield, 0.8 g. The color of an aqueous solution of the sodium salt was deep blue, which changed to dark green when acidified. Hypochlorite oxidation of this supposititious sodium sulfonate failed to yield any dye.

Summary

1. By the action of *o*- and *m*-nitrobenzoyl chlorides upon the zinc salt of 2-amino-5-methylphenyl mercaptan, the corresponding 2-nitrophenyl-benzothiazoles have been prepared.

2. Reduction of these nitro derivatives gave amines isomeric with dehydrothio-*p*-toluidine.

3. From the *m*-aminophenyl derivative, by hypochlorite oxidation of its sodium sulfonate, a direct cotton dye was prepared, presumably isomeric with Chloramine Yellow (Colour Index No. 814), but giving paler yellow shades. From the isomeric *o*-aminophenyl derivative, no similar dye could be obtained.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO OUR PREVIOUS ARTICLE¹ UNDER THIS TITLE AND REPLY TO DR. DE LASZLO²

By ALPHEUS W. SMITH, CECIL E. BOORD, CLYDE S. ADAMS AND CHARLES S. PEASE

RECEIVED AUGUST 4, 1927

PUBLISHED DECEMBER 10, 1927

The results contained in our previous paper have been challenged by Dr. de Laszlo with the contention that the absorption was in every case due to benzene. It is concluded "that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results as reported by these authors."

After a careful re-examination of ethylene chlorohydrin, methyl-*n*-amyl ether and ethyl ether in the light of these contentions we are compelled to admit that the results shown in our paper are due to benzene. It will be of general interest to know wherein this error arose.

As to cleanliness let it be said that it has been our unvarying practice to wash the absorption cells with chromic acid mixture after each run and that blank exposures through these same cells showed no absorption.

One comes then to the second alternative, namely, that the compounds examined contained benzene as a common impurity. A careful re-exami-

¹ Smith, Boord, Adams and Pease, *THIS JOURNAL*, 49, 1335 (1927).

² De Laszlo, *ibid.*, 49, 2106 (1927).

serve as a method of preparation for this latter substance, which, it should be noted, is that isomer most difficult to obtain by the synthetic series involving the isomeric 4-nitrodiphenamic acids and recently reported by us.⁷ The new method possesses the very real advantage of starting from the easily obtainable fluorene¹¹ instead of from phenanthrene, and of requiring only a few stages as compared with the diphenic acid procedure. Should the studies now in progress in this Laboratory show that other position isomers and substituents likewise yield only one of two possible fluorenone oximes, the utility of this method as a synthetic tool in the further elucidation of phenanthridone chemistry will be much increased.

Experimental Part

Fluorenone.—This was prepared according to Graebe and Rateneau¹² by oxidation of fluorene with sodium dichromate in glacial acetic acid solution. The fluorene was purified by distillation from 10% of its weight of solid potassium hydroxide; yield of fluorenone, 92%.

Fluorenone Oxime (I).—We employed the procedure of Spiegler,¹³ heating 8.5 g. of pure fluorenone with 6.6 g. of hydroxylamine hydrochloride in 80 cc. of 70% alcohol for three hours. The yield was 82% of the theoretical and the melting point 192–193° (195–196° corr.).

Beckmann Rearrangement of Fluorenone Oxime to Phenanthridone.—Five g. (1 mole) of fluorenone oxime was boiled under reflux for five hours with 7.5 g. (1.4 mole) of phosphorus pentachloride dissolved in 50 cc. (21 moles) of phosphorus oxychloride. The oxime rapidly dissolved in the mixture, imparting to it a pale orange color and liberating much hydrogen chloride. On completion of the reaction the phosphorous oxychloride was removed by distillation at ordinary pressure and the residual yellowish-red viscous oil was worked with water. This treatment soon changed it to a yellow powder which weighed 5.0 g., melted at 282–289° (corr.) and contained chlorine. One-half of this powder was boiled with 100 cc. of 50% sulfuric acid for one and one-half hours. After pouring onto ice, 2.1 g. of nearly white solid separated which, like the original, also melted at 282–289° (corr.). After three recrystallizations from glacial acetic acid, using Norit decolorizing carbon in the first, the product was pure white, free from chlorine and melted at 285–286° (293–294° corr.).

Although the appearance and behavior of this material assured us that it was phenanthridone, we confirmed this by the method of mixed melting points using for comparison phenanthridone prepared from diphenic acid in a previous research.¹⁴ Samples of known pure phenanthridone, our rearrangement product and a mixture of equal weights of these two in capillary tubes attached to the same thermometer melted simultaneously at 285–286° (293–294° corr.). This value is that recorded by Graebe for phenanthridone and substantiates the identity of the rearrangement product.

2-Nitrofluorene.—This substance was prepared by nitration of fluorene according to Diels;¹⁵ yield of 2-nitro isomer, 66%; m. p. 154–154.5° (corr.).

2-Nitrofluorenone.—Continuing Diels' method, the 2-nitrofluorene so obtained

¹¹ This hydrocarbon is sold by the Eastman Kodak Company.

¹² Graebe and Rateneau, *Ann.*, **279**, 258 (1894).

¹³ Spiegler, *Monatsh.*, **5**, 195 (1884).

¹⁴ Ref. 7, p. 1332.

¹⁵ Diels, *Ber.*, **34**, 1758 (1901).

was dissolved in acetic acid and oxidized with sodium dichromate; yield, 91%; m. p. 214–216° (219–221° corr.).

2-Nitrofluorenone Oxime (III or V).—Six g. of pure 2-nitrofluorenone was suspended in 240 cc. of alcohol and boiled for one and one-half hours with 3.5 g. of hydroxylamine hydrochloride dissolved in the least possible volume of water. The ketone soon dissolved and a much paler yellow, curdy material began to separate. After cooling and filtering, the product was washed free from chloride with alcohol and dried at 110°; yield, 75%; m. p., with decomposition, 262.5–263 (269–270° corr.).

Repeated attempts to purify the crude product by recrystallization from benzene, alcohol, glacial acetic acid or *n*-butanol led to the discovery that the more times it was recrystallized, the lower and wider became the melting-point range. At the time this observation was regarded as highly disturbing but from the results of our later work it seems probable that the lowering of the melting point of the oxime was due to progressive rearrangement to the Beckmann product under the influence of temperature and solvent. We finally concluded that attempts at purification were futile and used directly for analysis the product obtained from carefully purified ketone and melting sharply at 262.5–263° (uncorr.) with vigorous decomposition.

Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 64.97; H, 3.36; N, 11.68. Found: C, 64.69, 64.85; H, 3.40, 3.33; N, 12.21, 12.01.

Hydrolysis.—Saponification of the oxime with concentrated hydrochloric acid yielded a yellow solid, which was identified as 2-nitrofluorenone by mixed melting point, and a filtrate which gave on evaporation a solid which instantly reduced Tollens' reagent and gave Mulliken's¹⁸ color tests for hydroxylamine.

Beckmann Rearrangement of 2-Nitrofluorenone Oxime.—Twenty-three grams of 2-nitrofluorenone oxime was mixed with 34.5 g. of powdered phosphorus pentachloride and 200 cc. of phosphorus oxychloride and gently boiled under reflux for four hours. The liquid was divided into two equal portions and the solvent removed from each by distillation. The product from part A was allowed to crystallize, was then ground up in a mortar and allowed to stand in water for an hour. The residual lemon yellow solid was washed free from chloride and phosphate and after drying at 110° was found to melt at 153–173° and to contain chlorine. The residual solid from evaporation of part B was suspended in dry benzene for 39 hours; the benzene was then distilled off and the solid worked up with water as in part A. The product contained chlorine and melted at 152–193°.

Examination of Chlorine Compound from Part A.—A sample of the 153–173° product from part A was extracted with benzene, yielding a yellow solid melting at 150–185°. To remove possible nitrophenanthridone produced by hydrolysis we soaked the solid in strong alcoholic potassium hydroxide solution for a few minutes but failed to note the red color which accompanies the solution of 7-nitrophenanthridone under such circumstances. The washed solid was pale greenish-white in color and melted over the same range as before. It was analyzed for chlorine by the Carius method.

Anal. Calcd. for $C_{13}H_7ClN_2O_2$: Cl, 13.72; for $C_{13}H_7Cl_2N_2O_2$: 25.38. Found: Cl, 12.88, 13.09.

¹⁸ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1916, Vol. II, p. 30.

A sample of the product from part B was extracted with benzene in the same way and the product obtained was twice again recrystallized from benzene dried over sodium wire. The product melted at 155–170°. No alcoholic alkali treatment was employed. After drying at 50° in a vacuum the sample was analyzed for chlorine by the Carius method as before.

Anal. Calcd. for $C_{13}H_7ClN_2O_2$: Cl, 13.72; for $C_{13}H_7Cl_2N_2O_2$: 25.38. Found: Cl, 12.90, 13.00, 12.83, 12.99.

These data indicate that the materials from parts A and B are undoubtedly identical and that the chlorine content of samples purified by entirely different methods corresponds fairly well either to 2-nitrofluorenone-9-iminochloride (VII) or its rearrangement product 7-nitro-9-mesochlorophenanthridine (VIII) but not at all to 2-nitro-9,9-dichlorofluorene. The broad fusion range and its failure to change on repeated recrystallization suggest that we have an equilibrium mixture of the oxime chloride and its rearrangement product.

Conversion of Chlorine Compounds into 7-Nitrophenanthridone

Use of Chlorobenzene.—With the idea that a solvent more closely related to the substance might facilitate isomerization of one chloride to the other, 3 g. of crude chloride was boiled with 50 cc. of chlorobenzene. Nearly all of the solid dissolved and, after filtering and cooling, 0.50 g. of yellow solid giving only a slight test for chlorine and melting at 270–274° was deposited. This was purified by recrystallization from acetic acid, reprecipitation by sulfur dioxide from alcoholic potassium hydroxide solution and four subsequent crystallizations from acetic acid. The melting point of the yellow, chlorine-free substance was now 282–284° (uncorr.) and a mixture of it with known 7-nitrophenanthridone melted at the same temperature.

Use of Acetic Acid.—On the hypothesis that the production of 7-nitrophenanthridone from the chloride mixture would be facilitated by the presence of water in a mutual solvent, a sample of crude chloride melting at 150–170° was boiled with strong acetic acid for an hour. Hydrogen chloride was evolved and the solid obtained on cooling was free from halogen and melted at 285–292°. After purification from alcoholic alkali in the usual way, a bright yellow sample resulted, melting at 286–289° (uncorr.) and subliming in short, yellow needles like 7-nitrophenanthridone. The melting point of a sample of the latter was not depressed by admixture with the rearrangement product.

Use of 50% Sulfuric Acid.—With the original intention of hydrolyzing the oxime chloride to 2-nitrofluorenone, a sample of crude chloride was boiled with 50% c. p. sulfuric acid for over an hour. Hydrogen chloride was evolved as before, and upon dilution a yellow solid melting at 275–280° and free from halogen was obtained. Three recrystallizations from acetic acid raised the melting point to 284–285° (292–293° corr.). The melting point of its mixture with known 7-nitrophenanthridone melting at 284–285° (uncorr.) was the same.

Semiquantitative Study of Oxime Rearrangement.—Three g. of 2-nitrofluorenone oxime was refluxed for six hours with 4.5 g. of phosphorus pentachloride and 25 cc. of phosphorus oxychloride. The crude chlorine material obtained in the usual way melted at 150–170° (uncorr.) and weighed 3.11 g., corresponding to 96% of the theoretical. On boiling with 100 cc. of 50% sulfuric acid for one and one-half hours, dilution yielded 2.7 g. of crude product corresponding to 95% conversion of the chloride. After reprecipitation from alcoholic alkali it melted at 282–284° (290–292° corr.).

Anal. This was carried out on the rearrangement product melting at 284–285° (uncorr.). Calcd. for $C_{13}H_8N_2O_2$: C, 64.97; H, 3.36; N, 11.67. Found: C, 64.59, 64.51; H, 3.80, 3.89; N, 11.99, 11.99.

Summary

1. Fluorenone oxime has been shown to undergo a normal Beckmann rearrangement, yielding phenanthridone.
2. Oximation of 2-nitrofluorenone has been shown to yield mainly, if not entirely, one of two possible stereo-isomers.
3. Beckmann rearrangement of this 2-nitrofluorenone oxime to 7-nitrophenanthridone has been effected in yields of 90% and the method shown to be of preparative significance.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 17]

THE REARRANGEMENT OF ISOPROPYLETHYLENE TO TRIMETHYLETHYLENE AND THE PYROGENIC DECOMPOSITION OF PENTENE-2 AND TRIMETHYLETHYLENE

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One of the major subjects under investigation in this Laboratory is the influence of structure on the reactivity of atoms and groups in organic compounds. The problem is being studied from two points of view; in one the rates at which the members of a series of analogous compounds react with a fixed substance is being studied;² in the other the conditions are being investigated under which certain molecular rearrangements take place and under which definite bonds are severed through the influence of heat and catalytic agents. This paper contains the preliminary results obtained in the study of three amylenes from the second point of view.

A detailed study of the properties of the amylenes is of particular interest on account of the fact that certain of these hydrocarbons are formed in the cracking of petroleum and are now of importance as sources from which amyl alcohols are prepared on a large scale.

The amylenes selected for study were pentene-2, trimethylethylene, and *isopropylethylene*. These compounds can be prepared readily from easily available substances and possess structures that make possible the study of the effect of the position of the double bond on rearrangements and the severing of the molecules under the influence of heat. In *isopropylethylene* the double bond is in position 1, in pentene-2 in position

¹ From the thesis presented by Raymond Reuter in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1925. Grasselli Scholar in Chemistry 1924-1925.

² Norris and Ashdown, *THIS JOURNAL*, **47**, 837 (1925).

2 and in trimethylethylene there are two radicals in combination with one of the unsaturated carbon atoms.

The chemical reactivity of these isomers with inorganic acids varies greatly with their structure.³ The work described below shows that similar differences are observed when the isomers are subjected to the action of heat.

It was found that *isopropylethylene* rearranged to trimethylethylene to the extent of 10% when the vapor was passed through a silica tube containing alumina heated to 450° and the contact time was 1/4 minute. When aluminum sulfate was used as the catalyst 47% of the hydrocarbon underwent rearrangement. Phosphoric acid was found to facilitate the reaction but was not as efficient as aluminum sulfate.⁴

These results led to a detailed study of the influence of catalysts on the pyrogenic decomposition of *iso*-amyl alcohol, which furnishes the best method for the preparation of *isopropylethylene*. It was found that the presence of a catalyst and its nature affected markedly the product obtained. In the absence of a catalyst no rearrangement of the *isopropylethylene* produced was observed up to 450°; at higher temperatures partial rearrangement took place. When alumina was used the elimination of water took place at lower temperatures, but the catalyst did not materially alter the proportions in which the two isomers were formed. When, however, *iso*-amyl alcohol was dehydrated under the influence of aluminum sulfate or phosphoric acid, the proportion of trimethylethylene formed was largely increased. The results of three experiments are illustrations of these conclusions. At 375° with alumina (contact time 1/4 minute) 48% of the alcohol passed through the tube was decomposed and there was no rearrangement of the *isopropylethylene* formed. At the same temperature with aluminum sulfate, about 90% of the alcohol was decomposed and 70% of the product was trimethylethylene. With phosphoric acid a higher temperature was necessary to get appreciable dehydration; at 405°, 50% of the alcohol was decomposed and about 50% of the product was trimethylethylene.

The fact that catalysts of an acidic nature caused the rearrangement of *isopropylethylene* to trimethylethylene led to a detailed study of the action of sulfuric acid on the former. It was found that contrary to the behavior of other olefins of this type it could not be converted into a secondary alcohol. When the acid used was sufficiently strong to react with the hydrocarbon the chief product was a polymer. A small amount of tertiary amyl alcohol was formed from the trimethylethylene produced as the result of rearrangement.

³ Norris and Joubert, *THIS JOURNAL*, 49, 873 (1927).

⁴ Ipatiew, *Ber.*, 36, 2000 (1903), has studied the rearrangement of *isopropylethylene* at higher temperatures in the presence of alumina, but he reports no results with other catalysts.

Experiments were carried out to determine whether or not trimethylethylene would rearrange to isopropylethylene; under the conditions used by us no rearrangement was observed.

When pentene-2 was heated under a variety of conditions there was no evidence of the formation of branched-chain hydrocarbons.

The Pyrogenic Decomposition of Pentene-2 and Trimethylethylene

Pentene-2.—The hydrocarbon was passed through a silica tube at such a temperature and rate that it was not completely decomposed. These conditions were used to prevent excessive cracking of the primary products of decomposition. The reaction was studied in detail at 600° when the hydrocarbon was passed through the tube at such a rate that the contact time was 15 seconds. The interior of the silica tube was covered with a thin coating of carbon deposited from the gas before the decomposition was brought about. This was done to avoid the catalytic effect of the silica surface at the beginning of the experiment. Under these conditions about two-thirds of the hydrocarbon was decomposed.

The quantitative determination of the components of the complex mixture formed presented a difficult task. There are no satisfactory methods for the analysis of mixtures of paraffins, olefins or di-olefins. The methods used in this investigation gave results of sufficient accuracy, however, to warrant conclusions as to a probable mechanism of the decompositions studied.

The mixture of products obtained as the result of the decomposition of pentene-2 in a carefully carried out experiment at 600° consisted of ($1/3$) hydrocarbons having a molecular weight greater than pentene and ($2/3$) hydrocarbons of a lower molecular weight. The former, which appear to be unsaturated, have not yet been fully investigated.

The hydrocarbons having molecular weights lower than that of pentene were studied in some detail. The only saturated hydrocarbon found to be present was methane. There appeared to be no free hydrogen produced. The number of moles of methane was approximately equal to the sum of the number of moles of the other hydrocarbons present. This fact indicates that the decomposition consisted in the removal of a methyl group from the end of the chain of pentene-2⁵ and a similar removal in the case of the decomposition of the products formed as the cracking progressed. The carbon atom numbered 1 in pentene-2 or the one numbered 5 may be removed in this way. It is possible that the hydrocarbon decomposes in the two ways, but it is probable, for the following reasons, that in the decomposition the larger proportion of pentene loses carbon 5. In order to bring about the same percentage decomposition of trimethyl-

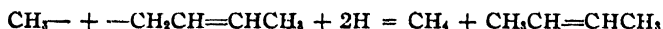
⁵ Gault and Altchidjian, *Ann. chim.*, [10] 2, 209 (1924), obtained a similar result with other hydrocarbons.

ethylene and pentene-2 a higher temperature is required in the case of the former. This fact indicates that it is more difficult to break the bond between a methyl radical and an unsaturated carbon atom than between the radical and a saturated atom.

If it is first assumed that the carbon atom numbered 5 is removed, the decomposition can be formulated as follows. The breaking of the bond results in the formation of two radicals



The addition of hydrogen to these radicals leads to the formation of methane and butene-2



The hydrogen necessary is produced as a result of the partial or complete decomposition of some hydrocarbon, since carbon is deposited in the tube. It is also formed during the conversion of the butylene radical into butadiene



The amounts of butene and butadiene-1,3 formed were approximately the same. The sum of the number of moles of butene and of butadiene was two-thirds of the number of moles of methane—a fact that indicates that a part of the butene radical, the primary product of decomposition, underwent subsequent cracking with the formation of methane. The presence of propylene and ethylene in the gas was demonstrated. It is possible that some propadiene was formed from the butylene, but if present its amount was too small for identification.

If a decomposition of pentene-2 takes place in which the carbon numbered 1 is split off, the reactions would be similar to those just described, with the difference that butene-1 instead of butene-2 would be formed. The method of analysis used in the work did not differentiate between these hydrocarbons. The butene present was converted into a butyl chloride by adding hydrochloric acid. Both butenes give 2-chlorobutane.

In the mixture of hydrocarbons showing molecular weights lower than the molecular weight of pentene the components were found to be present approximately in the molecular ratios: CH_4 , 100; C_4H_8 , 30; C_4H_6 , 27; C_3H_6 , 21; C_2H_4 , 15. The percentages by weight of the products obtained were approximately as follows: pentene-2 recovered, 33; hydrocarbons of higher molecular weight than that of pentene-2, 15; methane, 7.8; butadiene, 8; butene, 8; propylene, 4; ethylene, 2.

As has been noted, these conclusions are drawn from the results of the use of analytical methods which are in part but roughly quantitative. The determinations of methane were accurate as the usual combustion method was used. The determination of total unsaturated gases and of ethylene was also reasonably accurate. The butadiene was determined as the tetrabromide, which was isolated from the product formed as the result of the addition of bromine to the unsaturated compounds. The

tetrabromide was obtained in part by crystallization from the solvent used in the bromination and in part by distilling the bromides formed. The amounts of butylene and propylene were calculated from (1) the amounts of the several products formed in the fractionation of the dibromides and (2) the result of the fractionation of the chlorides produced by adding hydrochloric acid to the unsaturated hydrocarbons. The quantitative results in the case of butylene and propylene are, therefore, approximations only.

Trimethylethylene.—At 625° the extent of decomposition of trimethylethylene was about one-half that of pentene-2 at 600°, and at 650° the decomposition was slightly more. At the latter temperature about 70% of the hydrocarbon was decomposed when the contact time, as in the case of pentene-2, was 14-15 seconds. The product of decomposition as in the case of the isomer consisted of approximately $\frac{1}{3}$ hydrocarbons of higher and $\frac{2}{3}$ lower molecular weights. As before, no free hydrogen was formed and about $\frac{1}{2}$ of the gases was methane. In the examination of the products formed as a result of the decomposition of trimethylethylene, analyses were made for the proportion in which compounds

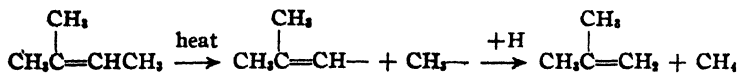
containing the grouping $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{array}$ were present. Such compounds react

rapidly with 60% sulfuric acid and with concentrated hydrochloric acid. About 30% of the gas produced in the reaction was rapidly absorbed by concentrated hydrochloric acid. About 20% of the gas consisted, therefore, of straight-chain unsaturated compounds. This latter conclusion is open to question, because the behavior of gaseous di-olefins with concentrated hydrochloric acid is not known. The 30% absorbed by the acid is, accordingly, a minimum figure for the olefins containing two methyl groups attached to an unsaturated carbon atom.

The liquid condensate from the decomposition was examined with 60% sulfuric acid for hydrocarbons of the type just mentioned. About 70% dissolved in acid of this strength. This fact leads to the conclusion that the higher hydrocarbons formed contained an appreciable amount of compounds having straight chains. No butadiene was found to be present in the gases.

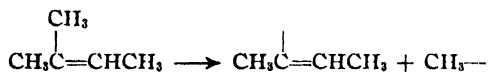
As in the case of pentene-2 the ethylene formed was approximately 10 molar per cent. of the methane formed; also, the amount of propylene was greater than that of ethylene.

The facts established by the work up to the present indicate that the decomposition in the case of trimethylethylene can be formulated in a way similar to that given in the case of pentene-2



The radical from *isobutene* cannot form a butadiene without the severing of a carbon-carbon bond followed by the recombination of the carbon atoms in a straight chain. As this kind of rearrangement is improbable, the fact that no butadiene-1,3 was found appears reasonable.

It is possible that the hydrocarbon may break as indicated below



The unsaturated radical could by loss of hydrogen form butadiene-1,2, which might rearrange to butadiene-1,3, although the only rearrangement yet observed is one which produces an acetylene derivative. The addition of hydrogen would produce butene-2, which by subsequent decompositions and recombinations would produce compounds with a straight chain. The butene formed would on subsequent decomposition be converted into propylene and ethylene.

The work on the two pentenes suggests that for a full understanding of the changes involved the pyrogenic decomposition of propylene, the butylenes and the dienes of low molecular weight should be studied. The investigation will be continued in this direction.

The work involved the development of analytical methods. As relatively large quantities of the hydrocarbons were made, an opportunity was offered to prepare samples in a high state of purity for the redetermination of certain physical properties. These results are given in detail in the experimental part of the paper.

Experimental Part

The Preparation of the Compounds Studied

Isopropylethylene.—A number of methods for the preparation of this hydrocarbon have been described.⁶ The directions for the method outlined briefly here are more specific than those previously given and are based on a detailed study of the effects of the various factors involved.

Isopropylethylene was prepared by passing *iso*-amyl alcohol over an alumina catalyst heated at 375–450°. When an electrically heated silica tube 4 feet long and 1 inch in internal diameter was used and the alcohol was passed through at the rate of 1.6 moles per hour (contact time 1/4 minute) about 50% of the alcohol was converted into amylene and most of the rest was recovered.

Since the *iso*-amyl alcohol used contained about 10% of active amyl alcohol it was necessary to remove from the crude amylene the unsymmetrical methylethylethylene formed and any trimethylethylene produced by rearrangement of *isopropylethylene*. This was accomplished by shaking the crude amylene for an hour at 30–35° with an equal volume of 60% sulfuric acid. The two substances were contained in a stout bottle closed by a tightly fitting rubber stopper which was wired in place and through which a thermometer passed. The bottle was attached to a shaking machine in the form of a

⁶ See Norris and Joubert, (ref. 3) for references—also Adams, Kamni and Marvel, *Univ. Ill. Bull.*, 16, No. 43, 10 (1919), and *THIS JOURNAL*, 40, 1950 (1918).

swing agitated by a motor. By placing an electric light bulb over the bottle and covering the machine with a towel the temperature could be maintained at 30–35°.

After the treatment a few cubic centimeters of the hydrocarbon should be tested by shaking at 30–35° with 4 volumes of the acid. If there is no change in volume in 15 minutes the separation of trimethylethylene and unsymmetrical methylethylethylene from the isopropylethylene is complete. If the decrease in volume is marked the treatment of the entire amount is repeated. The number of treatments is determined by the proportions in which the isomers are present.

The hydrocarbon purified in this way was washed with a dilute solution of sodium hydroxide, dried over calcium chloride, refluxed with sodium and distilled. The isopropylethylene obtained boiled at 20–21°.

After standing for four days, a hydrocarbon separated from the sulfuric acid solution used in the purification of isopropylethylene. It boiled at 153–155°, a small fraction boiled up to 160°. The main fraction was apparently the dimer of unsymmetrical methylethylethylene. Its index of refraction was n_D^{20} , 1.4382.

Trimethylethylene.—A number of methods have been given for the preparation of this hydrocarbon. The material used in this research was made by heating tertiary amyl alcohol with 46% sulfuric acid. The alcohol dissolves in acid of this strength and when the mixture is gently heated trimethylethylene separates and distills off.

One experiment gave the following results: 610 cc. (491 g.) of tertiary amyl alcohol was added to a cold mixture of 400 cc. of concentrated sulfuric acid and 800 cc. of water. On distillation 360 g. of hydrocarbon (92% of the theoretical amount) was obtained. A careful study of the product, which boiled at 36.7–38.7°, showed that it contained a small amount of unsymmetrical methylethylethylene.

Pentene-2.—This hydrocarbon was prepared by dehydrating the secondary amyl alcohol manufactured from petroleum. The alcohol is slowly dehydrated when one volume of it is heated with 1.5 volumes of 46% sulfuric acid. It is prepared most readily by using 60% acid. The yield is 90% of the hydrocarbon boiling between 36.5 and 40°.

Pentene-2 Dibromide.—This compound is described by Wagner and Saytzeff,⁷ who found that it boiled at 178° (uncorrected). It was prepared in order to ascertain its index of refraction, which was used in the examination of the material obtained as a result of the addition of bromine to the products of the cracking of pentene-2. It was made by adding to pentene-2 (b. p. 36.3–36.4°) bromine dissolved in 4 volumes of carbon tetrachloride at about –20°. The product was fractionated through a column. It was found to boil with slight decomposition at 180.2 to 180.8° (thermometer in vapor) at 754 mm. The fraction boiling at 180.2 to 180.5° had an index of refraction n_D^{10} 1.5149 and n_D^{20} 1.5098.

Trimethylethylene Dibromide.—The boiling point of this compound at atmospheric pressure and its index of refraction are not recorded. It was prepared in the way described above and was found to boil with slight decomposition at 170–173°. The fraction boiling at 170–172° had the index n_D^{20} 1.150 and the one boiling at 172–173°, n_D^{20} 1.511.

2-Chloropentane.—This compound has been prepared by Przewalski⁸ who reports the boiling point 96–97° and index $n_D^{19.5}$ 1.4062. Clough and Johns⁹ give 96° (760 mm.). It appeared advisable to examine carefully the product formed as a result of the addition of hydrogen chloride to pentene-2. The formation of two isomers is possible, 2-chloropentane and 3-chloropentane. The latter compound is reported to boil at 103–105°.

A very pure sample of pentene-2 was used, which boiled at 36.4° at 760 mm.

⁷ Wagner and Saytzeff, *Ann.*, 179, 307 (1875).

⁸ Przewalski, *Chem. Zentr.*, II, 793 (1909).

⁹ Clough and Johns, *Ind. Eng. Chem.*, 15, 1030 (1923).

When 20 cc. of the hydrocarbon was shaken with 9 volumes of concentrated hydrochloric acid for five and one-half hours at room temperature and then allowed to stand for fifteen hours, only about 40% of the hydrocarbon reacted. When a similar mixture was shaken for ten hours and left standing eight hours, almost two-thirds of the hydrocarbon was converted into chloride. The combined products were fractionated. The chloride obtained boiled at 96.87–96.96° at 759 mm.; index, n_D^{20} 1.4084. It is probable that the chloride formed in this way is in large part, or wholly, 2-chloropentane.

Determination of Physical Properties

Boiling Points.—Samples of the compounds studied, prepared in the ways just described, were subjected to fractional distillation. As the hydrocarbons boiled at low temperatures, precautions were taken to avoid superheating during distillation and efficient cooling of the vapors was secured.

Two fractionating columns were used. One, referred to as the 20-inch column, measured 18 inches from the bottom to the side neck and 1.25 inches in diameter. It was filled with pieces of 5 mm. glass tubing approximately 10 mm. long, set on end. The tower was furnished with a still head through which water could be circulated. A thermometer was so placed in the side neck that the mercury was completely immersed in vapor.

A similar column of similar construction 10 inches long and 0.5 inch in diameter was used when small amounts of liquid were fractionated.

The boiling points of the three hydrocarbons were determined with an Anschütz thermometer, graduated in fifths of a degree, which had been calibrated against a standard thermometer graduated in twentieths of a degree and calibrated at the Physikalisch-Technische Reichsanstalt. The boiling point of tertiary amyl alcohol was determined with a thermometer graduated in fifths of a degree and calibrated at the Reichsanstalt.

Melting Points.—The melting points of the hydrocarbons were determined by cooling 5cc. samples contained in 6-inch test-tubes with liquid air, and taking the temperature of the change in state with a pentane thermometer graduated in degrees.

The melting point of tertiary amyl alcohol was determined with a 125cc. sample which was frozen and then introduced into a carefully dried Dewar tube. The melting point was observed with a thermometer graduated in twentieths of a degree which had been calibrated at the Reichsanstalt.

Density.—The density determinations were made with samples contained in a 14cc. Sprengel tube or in a specific gravity bottle. Two determinations were made at 15 and at 25°. Single determinations were made at the other temperatures. A thermostat which remained constant to 0.005° was used for the measurements at 25°. A battery jar 6 by 8 inches was used as a thermostat at 15 and 20°. When the temperature of the room was within 2 degrees of that of the bath, the temperature

of the latter remained within 0.1 degree for fifteen minutes or more. The observations at 30° were made in a similar way, but the temperature of the bath remained within 0.1 degree for about five minutes only. The weights are reduced to a vacuum basis.

Index of Refraction.—An Abbé refractometer was used which was supplied with a calibrated thermometer graduated in whole degrees. Duplicate observations checked to 3 in the fourth decimal place.

Isopropylethylene.—The slow distillation of 200 cc. of the hydrocarbon prepared as described above showed that the boiling point of the pure compound lies between 20.0 and 20.2° at 759 mm. An 85cc. sample, separated between these limits, was redistilled at 759 mm. through the 10-inch column. The result was as follows: boiling point at the beginning of the distillation 20.0°; when 3 cc. had condensed 20.05°; total distillate 7 cc., 20.10°; 65 cc., 20.15°; 75 cc., 20.20°. About 80% of the hydrocarbon boiling within 0.2° distilled between 20.10 and 20.15°. It is safe to say that the boiling point of isopropylethylene at 759 mm. is $20.10 \pm 0.05^\circ$.

Pentene-2.—Two liters of the hydrocarbon boiling within 1 degree was fractionated with the 20-in. column at 771 mm. The portion measuring 500 cc. which boiled between 36.50 and 37.00° when redistilled yielded 375 cc. boiling between 36.70 and 36.90° and of this 265 cc. boiled between 36.70 and 36.75°. From these results the boiling point of pentene-2 appears to be $36.72 \pm 0.05^\circ$ at 771 mm.

The same sample was redistilled when the barometer registered 760 mm. The boiling point at this pressure was $36.39 \pm 0.03^\circ$.

Trimethylethylene.—In preparing the hydrocarbon to be used in the determination of physical properties a sample of tertiary amyl alcohol was used which boiled within 0.1° and melted within 1°. It was thought that a pure hydrocarbon might be produced in this way. The result proved that dehydration of the alcohol takes place in more than one way. The chief product is trimethylethylene but some unsymmetrical methylethylene, which is said to boil at 31–33°, is also formed. There is no way of separating the isomers by chemical means.

A sample of 1700 cc. of the mixed hydrocarbons was fractionated. The first distillation yielded 1450 cc. boiling between 36.7 and 38.7°. There was no break in the curve when volumes of the distillate were plotted against temperature. The hydrocarbon was redistilled six times, rejecting each time the lower-boiling fractions. It was only in the sixth distillation that a fraction was obtained which when redistilled boiled within the original temperature range. This fraction contained 300 cc. and boiled from 38.23 to 38.48°; 205 cc. boiled between 38.31 and 38.42°; and 145 cc. between 38.38 and 38.42°. These results indicate that trimethylethylene boils at $38.40 \pm 0.04^\circ$ at 759 mm. When redistilled at 770 mm. the hydrocarbon boiled at $38.78 \pm 0.04^\circ$.

Tertiary Amyl Alcohol.—A sample of the alcohol prepared from petroleum was used.¹⁰ The material was refluxed with barium oxide and fractionated with a 20-inch column. A fraction containing 785 cc. when refractionated at 755 mm. yielded 695 cc. boiling between 101.50 and 101.61°. Of this, 570 cc. boiled between 101.55 and 101.61°.

These results indicate that tertiary amyl alcohol boils at $101.58 \pm 0.03^\circ$ at 755 mm.

The sample when redistilled at 766 mm. boiled at $101.97 \pm 0.03^\circ$.

The results of the determination of physical properties are given in the following table.

¹⁰ We are indebted to A. D. Little, Inc., for the tertiary amyl alcohol used in this research.

TABLE I

PHYSICAL PROPERTIES OF PENTENE-2, ISOPROPYLETHYLENE, TRIMETHYLETHYLENE AND TERTIARY AMYL ALCOHOL

Pentene-2

B. p. $36.39 \pm 0.04^\circ$ at 760 mm. dt/dp , 0.030° per mm. (760-770) M. p. $-138 \pm 2^\circ$
 Density₄° 15°, 0.65551 20°, 0.65054 25°, 0.64537 ± 0.00003 30°, 0.64021
 n_D 5.3°, 1.3899 10°, 1.3868 15°, 1.3839 20°, 1.3808 30°, 1.3744

Isopropylethylene

B. p. $20.10 \pm 0.05^\circ$ at 760 mm. M. p., a thick sirup at -180°
 Density₄° 15°, 0.63197 ± 0.00002
 n_D 0°, 1.3762 10°, 1.3707 15°, 1.3675

Trimethylethylene

B. p. $38.42 \pm 0.04^\circ$ at 760 mm. dt/dp , 0.036° per mm. (760-770) M. p. $123 \pm 2^\circ$
 Density₄° 15°, 0.66708 ± 0.00002 25°, 0.65694 ± 0.00002
 n_D 10°, 1.3939 15°, 1.3908 20°, 1.3878 30°, 1.3814 35°, 1.3781

Tertiary Amyl Alcohol

B. p. $101.76 \pm 0.04^\circ$ at 760 mm. dt/dp , 0.035° per mm (755-765) M. p. $-11.9 \pm 0.5^\circ$
 Density₄° 15°, 0.81382 ± 0.00002 25°, 0.80475 ± 0.00002
 n_D 10°, 1.4104 15°, 1.4078 20°, 1.4052

The Action of Heat on Isopropylethylene, Trimethylethylene and Pentene-2

Apparatus.—The tube which was used for studying rearrangement and cracking was made of silica. It was four feet long, one inch in internal diameter, wound with No. 18 Chromel "A" resistance wire and covered with asbestos magnesia pipe covering. Three and one-half inches of the tube projected at the inlet end and 8.5 inches at the outlet end. This arrangement made possible the use of corks. The outlet end was connected with a four foot, quarter-inch spiral condenser made of copper. The receiver was a 250-cc. flask, set in ice water and connected with a gasometer.

Temperature measurements were made with two thermocouples. The junctions were so placed that they were 11 and 5 inches from the inlet and outlet ends, respectively, of the heated part of the tube. At the higher temperatures it was necessary to heat the inlet end of the tube with a flame in order to realize an even temperature throughout. In a tube of this length it is necessary to have two pyrometers in order to be sure of the temperature throughout the length of the tube.

Catalysts.—The substances used were (1) aluminum sulfate. A sample of commercial alum was heated in an iron dish until the water of crystallization was just driven off. The porous material was used in the form of small lumps. (2) Aluminum oxide. The material used was Merck's precipitated "aluminum hydroxide" powder. It was heated

for about ten minutes at 900° in the silica tube and then allowed to cool to the desired temperature in a stream of air. (3) Phosphoric acid. The catalyst was prepared by heating lumps of pumice which had been soaked in sirupy phosphoric acid.

Methods of Analysis.—In studying the rearrangement of *isopropyl*-ethylene into trimethylethylene it was necessary to devise a method for the quantitative determination of the two hydrocarbons in the presence of each other.

When no other substance is present, a determination of the index of refraction of the mixture serves as a reliable method of analysis. The index of a mixture of the two hydrocarbons in equal quantities was found to be within 0.5% of the mean of the indices of the two hydrocarbons. The same agreement was found in the case of mixtures of trimethylethylene and pentene-2.

A large number of experiments were carried out with the three hydrocarbons alone and with binary mixtures in an endeavor to develop a method of analysis based on the use of sulfuric acid. The effects of temperature, concentration of the acid, time of shaking and the relative amounts of the components in the mixtures were studied. The temperature finally selected was 33–35°. When small quantities of the materials were used they were contained in glass tubes $\frac{1}{2}$ inch in diameter and having a capacity of 20 cc. Changes in volume were measured by means of a millimeter scale. The tubes were shaken by hand in a bath, the temperature of which varied less than two degrees.

When larger quantities were used the materials were placed in oil sample bottles and shaken in a machine provided with an electric light bulb so placed that the temperature of the bottles covered with a towel measured nearly constant at 33–35°. Although the temperature is above the boiling point of *isopropylethylene*, a tightly fitting rubber stopper wired in place withstood the pressure, which at 35° was about 1.5 atmospheres. The best conditions for analysis of mixtures containing trimethylethylene are as follows. One volume of the mixture is shaken at 33–35° with 4 volumes of 60% sulfuric acid until the volume of the upper layer remains constant. When 3 to 4 cc. of the mixture of hydrocarbons is used solution of the trimethylethylene is complete in about fifteen minutes. The volume of the residual hydrocarbon layer is a measure of the amount of *isopropylethylene* or pentene-2 in the mixture.

When these conditions are used with mixtures, neither *isopropyl*-ethylene nor pentene-2 is attacked nor do they contain any polymer produced from trimethylethylene. The method was tested with mixtures containing as much as 85% of trimethylethylene and was found to be accurate within 3% at the higher concentrations and more accurate than this with lower percentages of the soluble hydrocarbon.

The great difference between the rates at which hydrochloric acid, contained in a concentrated aqueous solution, adds to olefins that yield tertiary chlorides and to those that yield secondary chlorides led to the study of the reactions with the expectation of developing a method of analyzing mixtures of these types of unsaturated hydrocarbons.

While the results did not lead to an exact analytical method, they showed that a close approximation could be obtained of the minimum amounts of trimethylethylene and *isobutene* present in mixtures of hydrocarbons which did not contain two radicals linked to an unsaturated carbon atom.

A mixture of air and the vapor of the hydrocarbons was analyzed in an apparatus for gas analysis. The mixture was treated first with concentrated hydrochloric acid and then with a solution of sodium hydroxide. The process was repeated as long as the volume of the mixture decreased appreciably. There are two sources of error in the method. The hydrocarbons that form secondary chlorides react very slowly with the acid; consequently the absorption does not come to a definite end when the hydrocarbons forming tertiary chlorides are removed. A second source of error is due to the fact that the tertiary chlorides produced have an appreciable vapor pressure at room temperature. One error tends to counteract the other; the results obtained are not exact but approximate the truth sufficiently to be useful.

The Results.—The hydrocarbons were heated at various temperatures up to that at which decomposition began. Incipient cracking was recognized by the evolution of gas. The results are given in Table II.

TABLE II

THE ACTION OF HEAT ON *ISOPROPYLETHYLENE*, *TRIMETHYLETHYLENE* AND *PENTENE-2*

No.	Hydro-carbon	Catalyst	Temp., °C.	Contact time, seconds	Rate, moles per hour	Hydro-carbon passed, moles	Hydro-carbon re-covered, %	Con-version, %	Gas, liters at 22°
1	<i>Isopropyl-ethylene</i>	Alumina	450	16	1.71	0.90	79	10 (trimethyl-ethylene)	0
2	<i>Isopropyl-ethylene</i>	Aluminum sulfate	425	16	1.81	.38	74	47 (trimethyl-ethylene)	0
3	<i>Isopropyl-ethylene</i>	Phosphoric acid	500	14	1.60	.36	90	29 (trimethyl-ethylene)	9
4	Hydrocarbon recovered from No. 3	Phosphoric acid	500	21	1.24	.31	91	15 (trimethyl-ethylene)	0
5	Trimethyl-ethylene	Alumina	450	21	1.30	.38	90	No <i>isopropyl-ethylene</i>	Trace
6	Trimethyl-ethylene	Phosphoric acid	500	20	1.27	.38	90	No <i>isopropyl-ethylene</i>	Trace
7	<i>Pentene-2</i>	Aluminum sulfate	350	15	2.1	.71	77	No <i>isopropyl-ethylene</i>	0
8	<i>Pentene-2</i>	Aluminum sulfate	450	16	1.7	.38	70	No isomers formed	0.1
9	<i>Pentene-2</i>	Phosphoric acid	525	12	2.0	.47	88	No isomers formed	0

Isopropylethylene rearranged to trimethylethylene, the extent of the change varying with the catalyst used. With one passage through the tube, alumina at 450° caused 10% conversion; phosphoric acid at 500°, 29%; and aluminum sulfate at 425°, 47%. The experiments in each case were carried out at the highest temperature at which cracking did not occur.

In experiment numbered 4 a mixture of *isopropylethylene* and trimethylethylene containing 29% of the latter was passed through the tube. Fifteen per cent. conversion took place, as the hydrocarbon recovered contained 44% of trimethylethylene.

Pentene-2 was not converted into any of its isomers under the conditions used.

The Rearrangement of *Isopropylethylene* to Trimethylethylene under the Influence of Sulfuric Acid.—Up to the present no one has succeeded in preparing the corresponding secondary alcohol from *isopropylethylene*, either by the addition of hydriodic acid¹¹ and subsequent hydrolysis or by treatment with sulfuric acid.³

The action of sulfuric acid on *isopropylethylene* was studied under conditions other than those already reported. Norris and Joubert did not observe any conditions under which *isopropylethylene* dissolved in sulfuric acid. We have found that when 1 cc. of the hydrocarbon is shaken with 1 cc. of 84% sulfuric acid at 35° for about ten minutes, a clear solution is obtained which almost immediately deposits an oil. Dilution of the clear solution as soon as formed yielded only a polymer which boiled at about 150°. When 69% sulfuric acid was used, the small amount of alcohol obtained proved to be tertiary amyl alcohol formed from the trimethylethylene produced as the result of the rearrangement of the *isopropylethylene*.

The experiment which showed that rearrangement takes place under the influence of sulfuric acid was carried out as follows: 100 cc. of carefully purified *isopropylethylene* (b. p. 20.1–20.2°) was shaken at 38° with 100 cc. of 60% sulfuric acid for one hour. The layer of hydrocarbon decreased 3.3% and that of acid increased 3.6%. The acid layer was neutralized with sodium hydroxide and distilled. Three cc. of an alcohol was obtained which boiled at 94–108°, three-fourths of it at 100–104°. Tertiary amyl alcohol boils at 102°. The alcohol dissolved in concentrated hydrochloric acid and was converted into a chloride which separated from the solution in about one minute. The *isopropylethylene* recovered was fractionated and yielded 3 cc. of a polymer which boiled below 160°.

The Rearrangement of *Isopropylethylene* to Trimethylethylene during the Dehydration of *Iso*-amyl Alcohol.—The fact that *isopropylethylene* rearranged to trimethylethylene under the influence of certain

¹¹ Wischnegradsky, *Ber.*, 10, 81 (1877) and *Ann.*, 190, 328 (1878).

catalysts led to a study of the effect of these catalysts when *iso*-amyl alcohol is used to prepare "amylene." The commercial variety of pentene sold under this name varies greatly in composition. The study of the reaction was extended with the view of developing methods for the direct preparation of either *isopropylethylene* or *trimethylethylene* from *iso*-amyl alcohol.

A number of the experiments carried out are listed in Table III. The results of the experiments numbered 1 to 3 show that when no catalyst is used the silica tube affects favorably the dehydration of the alcohol. When freshly glowing, 33% of the alcohol was changed to hydrocarbon. In the third experiment when the tube contained a slight deposit of carbon from two previous runs the conversion dropped to 9%. Increase in the temperature from 515 to 555° caused appreciable cracking to gaseous hydrocarbons. Experiments 4 and 5 show the influence of the rate of passage of the alcohol; doubling the rate decreased the conversion of alcohol to hydrocarbon from 41 to 36% and decreased slightly the percentage of the rearrangement of *isopropylethylene* to *trimethylethylene*.

TABLE III
DECOMPOSITION OF *ISO*-AMYL ALCOHOL BY HEAT

No	Catalyst	Temp, °C	Contact time, seconds	Rate, moles per hour	Moles alcohol passed	Alcohol obtained as hydrocarbon, %	Alcohol re-covered, %	<i>isopropylethylene</i> , %	Gas
1	None. Tube heated to redness before use	515	13	1.67	1.14	33	51	67	0.3
2	None. Tube from Exp. 1	555	12	1.87	1.12	17	66	79	4.0
3	None. Tube from Exp. 2	515	13	1.88	1.16	9	91	80	0.7
4	None. Tube heated to redness before use	515	12	1.80	1.26	36	57	62	.5
5	None. Tube heated to redness before use	515	19	0.97	1.21	41	53	67	.7
6	Al ₂ O ₃ (Merck's "Aluminum Hydroxide") heated to redness before use	375	17	1.56	1.25	48	38	90	5
7	Al ₂ O ₃ . Tube from Exp. 6	375	19	1.63	1.28	25	68	90	6
8	Al ₂ O ₃ . Heated to redness before use	450	13	1.66	1.27	52	26	90	3.9
9	Al ₂ O ₃ . Tube from Exp. 8	450	13	1.70	1.28	57	31	90	3.5
10	Al ₂ O ₃ . Tube from Exp. 9	450	13	1.65	1.29	58	30	90	3.4
11	Al ₂ O ₃ . Tube from Exp. 10	500	12	1.68	1.29	67	17	79	8.1
12	Al ₂ O ₃ . Tube from Exp. 11 after standing for 11 days	450	17	1.78	3.72	63	31	90	6.7
13	Al ₂ (SO ₄) ₃ . SO ₂ formed during exp.	345	15	1.48	0.81	57	15	21	0
14	Al ₂ (SO ₄) ₃ . Catalyst blackened during exp. Much H ₂ S formed	515	10	1.7	.5	25	.	22	6
15	Pumice with H ₃ PO ₄	405	14	1.43	.88	50	25	40	0
16	Tube from Exp. 15	500	11	1.68	.90	64	9	42	0
17	Tube from Exp. 16	505	12	1.67	.78	83	6	40	0

The effect of alumina as a catalyst is shown in experiments 6 to 12. Up to 450° it caused no rearrangement of the *isopropylethylene* produced

as the result of the dehydration of the alcohol. The hydrocarbon obtained contained 90% of *isopropylethylene*. The fusel oil *amyl alcohol* (b. p. 130–132°) used was shown by an optical test to contain 10% of active *amyl alcohol*. The latter yields when dehydrated unsymmetrical methyl-*ethylethylene*. At 375° the catalyst appears to decrease in activity with repeated use without reactivation by heating to redness. At 450° decrease in activity was not observed. At 500° cracking to gaseous hydrocarbons and some rearrangement to trimethylethylene take place.

Aluminum sulfate is the most active of the catalysts studied. At 345° dehydration of the alcohol took place to a greater extent than when alumina was used at 375°. It also was efficient in bringing about the rearrangement of *isopropylethylene*; the product contained but 21% of the latter hydrocarbon.

Phosphoric acid closely resembled alumina in its catalytic influence on the dehydration of the alcohol. It caused, however, more rearrangement of the *isopropylethylene* produced, but at the higher temperatures did not produce the cracking to gases observed when alumina was used.

The results show clearly that if it is desired to prepare *isopropylethylene* from *iso-amyl alcohol* by catalytic dehydration by heat, alumina should be used as the catalyst and the temperature should be near 450°. If it is desired to get the largest yield of trimethylethylene by the reaction, aluminum sulfate at 345° is the best catalyst.

Comparison of the results of the study of the rearrangement of *isopropylethylene* when the pure hydrocarbon is heated and when the rearrangement takes place during the dehydration of *iso-amyl alcohol* shows that the relative effectiveness of the catalysts is the same in both cases. The extent of rearrangement was greater in all cases when the alcohol was dehydrated.

The Cracking of Pentene-2 and Trimethylethylene.—The results obtained in the study of these hydrocarbons are given in Table IV.

The gases formed were analyzed as follows: (1) Total unsaturation by means of bromine water; (2) unsaturated hydrocarbons other than ethylene by means of 87% sulfuric acid; (3) methane by explosion with air after removal of unsaturated compounds; (4) total unsaturated compounds by fractionating the dibromides obtained when the gas was treated at –20 to –10° with bromine dissolved in carbon tetrachloride; (5) fractionation of the compounds formed as the result of the addition of concentrated hydrochloric acid.

(6) The liquid condensate was treated with 60% sulfuric acid for compounds containing two radicals linked to an unsaturated carbon atom and was (7) fractionated and the part boiling below 34° was (8) treated with bromine at –17 to –10° and the product fractionated and (9) with concentrated hydrochloric acid and the products fractionated.

TABLE IV
CRACKING OF PENTENE-2 AND TRIMETHYLETHYLENE

	Pentene-2			Trimethylethylene	
	1	2	3	1	2
Temperature, °C.	575°	600	600	625	650
Time of contact, seconds	12	14	14	14	13
Input rate, cc./min.	3.5	2.5	2.5	2.5	2.5
moles/hr.	2	1.4	1.4	1.4	1.4
Charge, cc.	205	200	140	140	140
g.	132	129	90+	92	92
moles	1.90	1.86	1.30	1.30	1.30
Recovered pentene, moles	1.2	0.9-0.6			0.3
fraction of charge	1/3	1/3			1/4
Decomposition products					
Temperature of condenser water, °C.	9	9	11	10	10
Liquid condensate	155	100	59	(About) 90	64
Charge by volume, %	77	50	42	(About) 64	46
Fractionation of liquid condensate					
% off at 30°	25	21			14
40°	96	71			59
70°		85			70
100°	99.5	89			78
150°	99.5+	95			
200°		98			93
Gas, liters at 22°	9	33	28	15	27
liters per 100 cc. charge	4.4	16	20	11	19
moles per mole charge	0.19	0.72	0.88	0.48	0.85
Individual hydrocarbons produced					
Methane, moles/mole charge	0.01	0.34	0.31	0.26	0.46
Ethylene, moles/mole charge	.005	.05		.024	.047
Propylene, moles/mole charge	.02-	.07+		Greater than ethylene	
Butylene, moles/mole charge	.1	0.06-0.13		(?) 0.11	
Hexylene, 50-75° cut		0.03-			
Butadiene, 50-75° cut	.003	0.13-0.09		Little or none	Little or none
Hydrocarbons available for tertiary alcohol formation					
% in gas (by HCl)	Absent	Absent	5-10	30	30
% in liquid condensate (by 60% H ₂ SO ₄ solution), 33°, 15 min.	Absent	Trace (?)	69

Summary

1. The rearrangement of *isopropylethylene* to trimethylethylene produced by heat is markedly affected by catalysts. The efficiency increases in the order alumina, phosphoric acid, aluminum sulfate.

2. The rearrangement of *isopropylethylene* to trimethylethylene which takes place when *iso*-amyl alcohol is dehydrated by heat is slightly greater than when the hydrocarbon is heated. The efficiency of the catalysts in causing rearrangement is in the same order as in (1) above.

(3) Under the conditions used trimethylethylene did not rearrange to *isopropylethylene*.

(4) When pentene-2 was heated the results showed that no branched-chain hydrocarbons were formed.

(5) The pyrogenic decomposition of pentene-2 and trimethylethylene yielded gaseous and liquid hydrocarbons which were analyzed quanti-

tatively for the following hydrocarbons: methane, butene, butadiene, propylene, ethylene, higher hydrocarbons. The results lead to an interpretation of the mechanism of the decompositions.

(6) *Isopropylethylene* is stable toward diluted sulfuric acid but can be made to rearrange to trimethylethylene to a slight extent by the action of acid of such a concentration that polymerization does not take place appreciably.

(7) The boiling point, melting point, densities at various temperatures and index of refraction of trimethylethylene, pentene-2, *isopropylethylene* and tertiary amyl alcohol were redetermined with carefully purified material.

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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. II. SECOND CONTRIBUTION ON THE RELATIVE REACTIVITIES OF THE HYDROXYL-HYDROGEN ATOMS IN CERTAIN ALCOHOLS

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In a former paper² from this Laboratory the results were given of the study of the rates at which certain alcohols react with *p*-nitrobenzoyl chloride, and it was shown that the rates, which varied greatly, could be taken as a measure of the relative reactivities of the hydroxyl-hydrogen atoms in these alcohols. As certain striking relationships were indicated from the results obtained with the eleven alcohols investigated, the work was continued and eighteen additional compounds were studied. The alcohols were so selected that the results would show the influence of structure on the reactivity of the hydroxyl-hydrogen atom, especially as this reactivity is affected by lengthening of the carbon chain and by the position of a side chain with reference to the hydroxyl group.

Sufficient data have been obtained from the investigation of these twenty-nine alcohols to warrant definite conclusions. The results are in accord with the well-known qualitative differences in chemical behavior between the several types of alcohols; but they have, in addition, a quantitative significance, and throw some light on the change in the atomic bonding between oxygen and hydrogen produced by changes in the structure of the radical with which the hydroxyl group is combined.

¹ From the thesis of Frank Cortese, Grasselli Fellow in Chemistry, 1925-1926, presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1926.

² Norris and Ashdown, *THIS JOURNAL*, **47**, 837 (1925).

The effect of the substitution of a hydrogen atom by a methyl radical in a series of normal alcohols is noteworthy. For example, such replacement of an α -hydrogen atom in ethyl, propyl, butyl and amyl alcohols, respectively, caused a decrease in the reactivity of hydroxyl-hydrogen atom of the same order of magnitude in the four cases. Similar results were obtained when the methyl radical was in the beta, gamma and delta positions, although the percentage effect differed in the various positions.

Objections have been raised to the use of reaction velocities in the comparison of the chemical behavior of compounds. These objections are based upon the fact that the rate at which a reaction proceeds is markedly affected by conditions, some of which are not under control, such as, for example, the presence of unrecognized catalytic agents. The relationships indicated above were drawn from the results of the study of a large number of independent reactions and could not have been obtained if unrecognized factors that influenced the results were involved. An important deduction from the work is, therefore, that velocity constants when determined under fixed conditions can be used in the quantitative interpretation of chemical behavior.

All synthetic methods used in organic chemistry are based on the reactivities of the atoms involved in the changes which result in the desired syntheses. Quantitative measurements of these reactivities are largely lacking and any additional knowledge in this field will advance the science from the point of view of synthesis, and will be useful in enlarging our knowledge of bonding between atoms. The work described in this paper will make possible a more intelligent use of alcohols in syntheses involving the hydroxyl-hydrogen atoms of these compounds, and will be helpful in interpreting the effect of structure on the lability of the hydrogen-oxygen bond.

The methods used in the determination of the velocity constants of the alcohols were identical with those reported in the earlier communication.² The constant for *n*-butyl alcohol was redetermined in order to find out if the conditions of experimentation were identical with those used in the earlier investigation. The results checked the value previously obtained within the limit of accuracy of the work. In order to facilitate comparisons the constants of all the alcohols studied up to the present are given in Table I. The alcohols reported on in this paper are listed in Table II.

The study of the results given in Table I leads to the following conclusions.

(1) The lengthening of the carbon chain in normal primary alcohols results in a decrease in the reactivity of the hydroxyl-hydrogen in the first three members of the series; the constant increases progressively with the next three members and then decreases again.

TABLE I

SECOND ORDER VELOCITY CONSTANTS FOR THE REACTIONS BETWEEN ALCOHOLS AND *p*-NITROBENZOYL CHLORIDE

Temperature, 25°. Concentration of each reactant 1 mole in 1000 g. of ether taken as unity. Time in hours.

Normal primary alcohols	<i>k</i>	Secondary alcohols	<i>k</i>
Methanol.....	0.184	Propanol-2.....	0.010
Ethanol.....	.085	Butanol-2.....	.0074
Propanol-1.....	.066	Pentanol-2.....	.0059
Butanol-1.....	.074	Hexanol-2.....	.0065
Pentanol-1.....	.079	Pentanol-3.....	.0036
Hexanol-1.....	.085	Heptanol-4.....	.0027
Heptanol-1.....	.069		
Primary alcohols with a branched chain		Tertiary alcohols	
Methyl-2-propanol-1.....	0.031	Methyl-2-propanol-2.....	0.0027
Methyl-2-butanol-1.....	.036	Methyl-2-butanol-2.....	.0025
Methyl-2-pentanol-1.....	.034	Methyl-3-pentanol-3.....	.0014
Methyl-3-butanol-1.....	.073	Aromatic alcohols	
Methyl-3-pentanol-1.....	.077	Benzyl.....	0.017
Methyl-3-hexanol-1.....	.075	β -Phenylethyl.....	.040
Methyl-4-pentanol-1.....	.068	γ -Phenylpropyl.....	.020
		α -Phenylethyl.....	.00052
		α -Phenylpropyl.....	.00050
		α -Phenylbutyl.....	.00050

In the case of the secondary alcohols with the hydroxyl group in position 2 the constant decreases with the first three members of the series and then increases.

(2) The introduction of a methyl radical as a side chain in primary alcohols has a marked effect on the constant. This effect is greatest in position 1; it decreases as we pass to positions 2 and 3 and begins to increase in position 4. The alternations in this effect are similar to, though greater than, those brought about by lengthening the chain—the periodicity is in cycles of 3.

(3) The percentage reduction in the constant brought about by the replacement of a hydrogen atom in position 1 by a methyl radical is of the same order of magnitude whatever the length of the chain. The constant of *isopropyl* alcohol is 11.7% of the constant of *ethyl* alcohol; that of secondary *butyl* alcohol is 11.2% of the constant of *n-propyl* alcohol; the constant of *pentanol-2* is 8% that of *n-butyl* alcohol; and the constant of *hexanol-2* is 8.2% that of *amyl* alcohol.

(4) When a methyl radical replaces a hydrogen atom in position 2 its effect on the constant is much less. The constant of *isobutyl* alcohol is 46.9% of that of *n-propyl* alcohol; the constant of *methyl-2-butanol-1* is 48.6% that of *n-butyl* alcohol; and the constant of *methyl-2-pentanol-1* is 44.3% that of *n-amyl* alcohol.

(5) When a methyl radical replaces a hydrogen atom in position 3 the effect almost disappears. The constant of *iso-amyl* alcohol is 98%

that of *n*-butyl alcohol; and the constant of methyl-3-pentanol-1 is 97% that of *n*-amyl alcohol.

(6) When a methyl radical replaces a hydrogen atom in position 4 the effect now begins to increase. The constant of methyl-4-pentanol-1 is 86% that of *n*-amyl alcohol.

(7) The relationships between the constants of primary and secondary alcohols containing the same number of carbon atoms are as follows. The constant of the secondary alcohols containing 3, 4, 5 and 6 carbon atoms are, respectively, 15.8, 10.0, 7.5 and 7.6% those of the corresponding primary alcohols. In this case the effect increases with increasing molecular weight in the case of the first three members of the series.

(8) The relationships between the constants of tertiary and primary alcohols containing four and five carbon atoms are, respectively, 3.7 and 3.2%.

(9) The effect of the position of the hydroxyl group in a straight chain of carbon atoms is great. The constants of pentanol-1, pentanol-2 and pentanol-3 are in the ratio 1 to 0.075 to 0.045.

(10) In the case of the aromatic alcohols there is an alternation in the value of the constant as the phenyl radical is removed from the hydroxyl group. The depression of reactivity produced by the replacement of a hydrogen atom by phenyl is so great that the secondary alcohols containing this group in position 1 had the smallest constants measured.

The striking relationships between the constants of alcohols of similar structure indicate clearly that the results are significant in regard to the effect of the position of a substituent on the hydrogen bond in alcohols. It is hoped to interpret later the results in terms of the electronic theory of the bonding of atoms in organic compounds. Further work must be done, however, before this is attempted. The relationships indicated hold when the hydroxyl-hydrogen is replaced by the *p*-nitrobenzoyl radical. It is possible that they may be found to be different when another atom or group replaces this hydrogen atom. The speed with which two molecules interact depends at least in part on the tendency of the atoms eliminated to unite and the tendency of the radicals formed to combine with each other. It is interesting to note in this connection that the velocity constant of *isopropyl* alcohol is 11.7% of that of ethyl alcohol when measured by *p*-nitrobenzoyl chloride as a second order reaction in ethereal solution, and that the velocity constant of *isopropyl* alcohol is 9.4% of that of ethyl alcohol when measured as first order reactions by diphenyl-chloromethane dissolved in a large excess of the respective alcohols.

Work is now in progress on the study of rates at which alcohols react with sodium and with potassium. As the result of this type of reaction, hydrogen is eliminated and the hydroxyl-hydrogen is replaced by a strongly electropositive metal.

TABLE II
PREPARATION AND PROPERTIES OF THE ALCOHOLS USED*

Alcohol	Substances used in preparation	Crude alcohol % B. p. (°C. at 760 mm.) yield	Fractionated alcohol % B. p. (°C. at 760 mm.)	Fractionation of purified alcohol from final b. p. in literature and references ()	Density, 25°/4°; density in lit. crature and references ()	N _D ²⁰ ; index in lit. crature and references ()		
Pentanol-1	Butyl bromide	47	134-144	300	52	138.0-138.1	0.8110	1.4077
	Trioxymethylene						.8106(2)	1.4114(15°)(3)
							.8153	1.4162
Hexanol-1	Butyl bromide	68	150-160	191	28	157.6-157.7	.8154(4)	
	Ethylene oxide					157.3-157.6(2)	.8129(2)	
							.8187	1.4224
Heptanol-1	From Eastman			100	24	175.8-176.2	.8185(5)	1.4222(5)
	Kodak Company		172.8-175.8				.8152	1.4087
Methyl-2-butanol-1	Sec. butyl bromide			295	64	129.4	.8155(11)	
	Trioxymethylene	59	124-135			129.4(11)	.8192	1.4180
				142	16	147.9-148.1	.8191(15)	1.4182 (at 19°)
						147.9(16)	(17)	
	Sec. amyl bromide					147.8(15)	.8044	1.4046
Methyl-3-butanol-1	Trioxymethylene	70	143-150	129	26	132.0-132.1	.8238(6)	
	Isopropyl bromide	30	125-138			131.9(6)	.8205	1.4177
	Ethylene oxide			74	12	153.7-154.1	.8226(19)	
Methyl-3-pentanol-1	Sec. butyl bromide	36	149-157			154.1(18)	.8245	1.4246
	Ethylene oxide			82	8	171.7-172.7	.8239(21)	1.4219(20°)(21)
Methyl-3-hexanol-1	Sec. amyl bromide	36	150-173			173(21)	.8110	1.4134
	Ethylene oxide			155	12	151.8-152.8	.8156(12)	1.5152(20°)(12)
Methyl-4-pentanol-1	Isobutyl bromide	45	142-157			153(12)	.8068	1.4048
	Ethylene oxide			300	40	119.16-119.26	.8088(10)	1.4043(9)
Pentanol-2	From Standard					119.2(10)	.8048(9)	
	Oil Co.	35	118-120			119.5(9)		

TABLE II (Concluded)

Alcohol	Substances used in preparation	Crude alcohol % yield	B. p. (°C. at 760 mm.)	Gr. of alcohol fractionated	Gr. of purified alcohol from final fractionation	B. p. (°C. at 760 mm.) of purified alcohol; b. p. in literature and references ()	Density, 25°/4°; density in literature and references ()	N ^o . index in literature and references ()
Hexanol-2	Butyl bromide	28	133-142	90	8	140.0-140.4	0.8044	1.4136
	Acetaldehyde					140.1(13)	d ₄ ⁰ .8287(14)	1.4140(18°)
							d ₄ ²⁵ .8141(14)	
Pentanol-3	Ethyl bromide			92	24	115.8-116.0	.8154	1.4079
	Ethyl formate	52	112-118			115.6(9)	.8154(9)	1.4077(9)
Heptanol-4	Propyl bromide			150	32	155.9-156.0	.8156	1.4184
	Ethyl formate	64	150-153			155.4(9)	.8130(9)	1.4178(9)
Methyl-2-butanol-2	From A. D. Little, Inc. Prepared by Raymond Reuter(7)			600		101.7-101.8(7)	.80475(7)	1.4024
Methyl-3-pentanol-3	Ethyl bromide			116	28	101.5-102(8)	.80452(8)	
	Ethyl acetate	57	117-123			122.8-123.0	.8233	1.4166
α-Phenylethyl				57	16	122.4-123.4(20)	.8194(20)	
	Acetophenone	36	94-95(12 mm.)			94-95(12 mm.)	1.0119	1.5244
α-Phenylpropyl	Ethyl bromide			209	100	94(12 mm.)(22)	d ₄ ¹⁵ 1.008(23)	1.526(15°)(23)
	Benzaldehyde	77	100-111(15 mm.)			106-108(15 mm.)	0.9915	1.5124
						63.2-63.4(0.5 mm.)	.9925(25)	1.5204
α-Phenylbutyl	Propyl bromide			195	64	108-110(15 mm.)(24)		
	Benzaldehyde	65	117-125(15 mm.)			78.0-78.2(0.5 mm.)	.9697	1.5191(13.7°)
						113-115(10 mm.)(26)	d ₄ ¹⁵ .9861(26)	

* Note: The values taken from the literature were the best ones found, the methods of preparation and purification always being taken as the criteria of purity. The figures in parentheses refer to the citations at the end of the table.

TABLE III (Concluded)

Alcohol	No. of vations	Time to last ob- servation, hours	% Con- version at last observation	Greatest % deviation of any observation from mean	Constant	Average
Pentanol-2	8	10	5.4	4	.0058	
	8	10	5.4	5	.0059	.0059
Hexanol-2	7	11	6.7	4	.0065	
	7	11	6.5	3	.0065	.0065
Pentanol-3	8	11	3.2	2	.0037	
	8	11	3.8	8	.0035	.0036
Heptanol-4	7	8	2.4	4	.0027	
	7	8	2.3	4	.0027	.0027
Methyl-2-butanol-2	6	10	2.6	0	.0025	
	6	10	2.5	4	.0025	.0025
Methyl-3-pentanol-3	7	11	1.5	7	.0014	
	7	11	1.5	0	.0014	.0014
α -Phenylethyl	7	169	7.4	8	.00052	
	7	169	7.5	4	.00052	.00052
α -Phenylpropyl	8	198	8.7	6	.00049	
	8	198	8.5	10	.00050	.00050
α -Phenylbutyl	8	220	10.1	6	.00050	.00050

* Note: The extent to which the reactions had proceeded at any time was determined by the titration of the hydrochloric acid produced. The values given above for the per cent. conversion have been corrected for the small amount of hydrochloric acid formed by hydrolysis from the acyl chloride during the titration.

It was found with these alcohols, as was the case with those studied earlier, that the velocity constant decreased slowly in value after a certain percentage of the alcohol had been converted into ester. The values given in Table III are calculated from the results obtained up to the time when the decrease in the constant began. It can be seen from the table that in the case of primary alcohols the reaction fulfilled the requirements of one of the second order up to from 20 to 35% conversion to ester. In the case of secondary alcohols the decrease in the constant began when from 4 to 7% conversion had taken place; and in the case of tertiary alcohols the change occurred at a lower conversion.

It is probable that the reaction may not be one of the second order—that a more complex mechanism is involved—but the results show that at the beginning of the reaction the requirements of the equation for a reaction of this type are fulfilled; and comparisons under these circumstances are justified. It should be noted that the method of calculating second-order velocity constants has been shown in the past to give real constants only when reactions are carried out at very low concentrations—

in certain cases as low as 0.02 normal. Further, constants calculated from results obtained at different concentrations do not agree except when the concentrations used are very small.

It was impossible to determine with a reasonable degree of accuracy the velocity constants of the reactions reported in this paper at lower concentrations than 0.2 *N*. The degree of accuracy of the analytical methods used and the sources of error that could not be eliminated made work at lower concentrations inadvisable.

In order to study the influence of change in concentration in the constants, experiments were carried out with four alcohols with solutions made by dissolving, respectively, 1, 0.5 and 0.2 moles of the alcohols in 1000 g. of ether. The values are given in Table IV.

TABLE IV

EFFECT OF CONCENTRATION ON THE VELOCITY CONSTANT OF THE REACTION BETWEEN ALCOHOLS AND *p*-NITROBENZOYL CHLORIDE DISSOLVED IN ETHER

Alcohol	Moles of each reactant in 1000 g of ether	<i>k</i>
Methyl-2-butanol-1	1.0	0.036
Methyl-2-butanol-1	0.5	.019
Methyl-3-butanol-1	1.0	.073
Methyl-3-butanol-1	0.5	.032
Methyl-3-butanol-1	.2	.011
<i>n</i> -Amyl	1.1	.079
<i>n</i> -Amyl	0.5	.048
<i>n</i> -Amyl	.2	.034
<i>n</i> -Hexyl	1	.085
<i>n</i> -Hexyl	0.5	.054
<i>n</i> -Hexyl	.2	.035

The constants tabulated show in all cases that the values decrease rapidly with decreasing concentration. It is important to note, however, that the order in which the alcohols stand, as measured by the reactivity of their hydroxyl-hydrogen atoms, is the same irrespective of the concentration at which they are compared. The earlier results with methyl and ethyl alcohols led to the same conclusion.

The cause of the progressive change in velocity constant is being studied with the hope of elucidating the mechanism of the reactions involved. It is possible that the reactions are reversible or that the ester and hydrochloric acid formed react. If either is the case, the use of the usual expression for calculating a second-order velocity constant is warranted only in the early stages of the reaction before the secondary reaction becomes significant. The constants given are based on this assumption.

Summary

1. The second order velocity constants for the reaction between *p*-nitrobenzoyl chloride and the following alcohols have been determined:

pentanol-1, hexanol-1, heptanol-1, methyl-2-butanol-1, methyl-2-pentanol-1, methyl-3-butanol-1, methyl-3-pentanol-1, methyl-3-hexanol-1, methyl-4-pentanol-1, pentanol-2, hexanol-2, pentanol-3, heptanol-4, methyl-2-butanol-2, methyl-3-pentanol-3, α -phenylethyl, α -phenylpropyl and α -phenylbutyl alcohols.

2. The results obtained, together with those from an earlier investigation of the lower fatty alcohols, make possible definite conclusions as to the effect of structure on the reactivity of the hydroxyl-hydrogen atoms of alcohols.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY
No. 554]

RESEARCHES ON QUINAZOLINES. XXXVIII. THE SYNTHESIS OF SOME NEW ANALOGS OF CINCHOPHEN AND INTERMEDIATE PRODUCTS

BY MARSTON TAYLOR BOGERT AND EUGENE MILLER MCCOLM¹

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Our knowledge of the pharmacodynamics of the quinazoline group is scattering, fragmentary and meager. It, therefore, seems to us worth while to endeavor to contribute something to this field, not only with the object of throwing additional light upon the connection between chemical constitution and physiological effects, but also in the hope of discovering new compounds of therapeutic value. In this undertaking we have been so fortunate as to enlist the valuable coöperation of two distinguished pharmacologists, Professors Arthur D. Hirschfelder, of the University of Minnesota, and Elbert W. Rockwood, of the State University of Iowa, whose investigations will be published in appropriate journals.

The syntheses recorded in this paper were for the purpose of obtaining quinazoline derivatives of cinchophen (atophan) type, carrying a carboxyl group in Position 4 and hydroxylated phenyls in Position 2, since the preliminary pharmacological examination of the di-ammonium salt of 2-phenylquinazoline-4,2'-dicarboxylic acid, synthesized by Bogert and Nabenhauer,² had given results which looked both interesting and promising.

From these carboxylic acids, ethyl esters also were prepared, giving compounds analogous to acitrin; while the 2-hydroxyphenyl-4-carboxylic acids are intermediate between our 4,2'-dicarboxylic acid and the well-known hexophan of the cinchophen series.

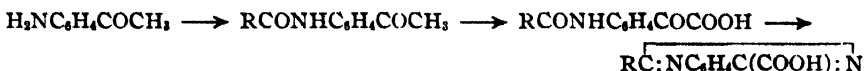
These 2-hydroxyphenylquinazolines were synthesized because Kalle and

¹ This research was made possible by a generous grant from the Sigma Xi Foundation, for whose assistance we are most grateful.—M. T. B. and E. M. McC.

² Bogert and Nabenhauer, *THIS JOURNAL*, **46**, 1702 (1924).

Company took out a patent³ in 1915 for the manufacture of 2-hydroxy-phenylquinoline-4-carboxylic acids, in which they claimed that their action was similar to that of cinchophen, but without its bitter taste or irritating action upon the stomach, that the hydroxyl groups endowed them with pronounced antiseptic and antipyretic properties, that they exhibited a definite beneficial action against the plasmodia of malaria similar to that of quinine and that they were also of value in the treatment of pertussis.

The plan of synthesis followed that developed by Bogert and Nabenhauer,² and consisted in the preparation of the substituted *o*-amino-acetophenone, oxidation of this to the corresponding isatinic acid and the conversion of the latter into the quinazoline derivative by heating it with alcoholic ammonia under pressure.



Experimental Part

Quinazoline itself, required for an investigation which will be reported later, was prepared from *o*-nitrobenzaldiformamide by a modification of the excellent method of Riedel.⁴ The yield of pure *o*-nitrobenzaldiformamide (m. p. 178°, corr.) was 70%. It was converted into quinazoline as follows.

To a mixture of 20 g. of finely pulverized diformamide with 60 g. of zinc dust, there were slowly added 240 g. of cracked ice and then 80 g. of glacial acetic acid, while the mixture was being well shaken. When a 25% solution of acetic acid was employed, with external cooling instead of using cracked ice in the mixture, local superheating occurred and the yield of quinazoline was much less. After the reduction had been completed by shaking the mixture for about an hour, with frequent additions of small amounts of zinc dust, the acid solution was filtered from the excess of zinc dust. Sufficient caustic alkali (400 cc. of 50% sodium hydroxide solution) was added to this filtrate to redissolve the zinc hydroxide precipitated, the alkaline solution was extracted repeatedly with ether, the ethereal extracts dried over sodium sulfate, the solvent evaporated and the residual quinazoline purified by crystallization from petroleum ether or by distillation; yield of pure product, m. p. 48°, 10 g. or 93%.

Attempts were made to use a crude *o*-nitrobenzaldehyde, containing some of the *m*-nitro isomer, in place of the pure *o*-compound, but it was found that this necessitated a laborious separation of the formamide condensation products and it was, therefore, abandoned.

Salicyl Chloride was prepared from sodium salicylate and thionyl chloride by the process of Kopetschni and Karczag,⁵ which was found preferable to that of Wolfenstein.⁶ *o*-(*o*-Nitrobenzoylamino)-acetophenone, $\text{O}_2\text{NC}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{COCH}_3$.—To a vigor-

³ Kalle and Co., Ger. pat. 284,233 (1915).

⁴ Riedel, Ger. pat. 174,941 (1905).

⁵ Kopetschni and Karczag, *Ber.*, 47, 235 (1914).

⁶ Wolfenstein, Ger. pat. 284,161 (1915).

ously agitated dispersion of 8 g. of *o*-amino-acetophenone in 100 cc. of a 10% aqueous sodium hydroxide solution, there was added 20 g. of *o*-nitrobenzoyl chloride. The mixture was thoroughly shaken while the flask was well cooled externally. When the odor of the acid chloride was no longer perceptible, the precipitate was collected and crystallized from alcohol. Colorless needles were obtained, m. p. 156° (corr.); yield, 13 g. or 78%.

Anal. Calcd. for $C_{15}H_{11}O_4N_2$: C, 63.37; H, 4.26. Found: C, 63.75; H, 4.45.

o-(*m*-Nitrobenzoylamino)-acetophenone, prepared in a similar manner and in approximately the same yield, formed colorless needles, m. p. 170° (corr.).

Anal. Calcd. for $C_{15}H_{11}O_4N_2$: C, 63.37; H, 4.26. Found: C, 63.32; H, 4.30.

o-Salicylamino-acetophenone, $HOC_6H_4CONHC_6H_4COCH_3$.—A benzene solution of 20 g. of salicyl chloride and 15 g. of *o*-amino-acetophenone was refluxed until the evolution of HCl ceased. The solution gradually darkened during this heating and, when finally permitted to cool, a mass of brown needles separated which when decolorized and crystallized from alcohol appeared in colorless needles, m. p. 135° (corr.); yield, 17 g. or 59%.

Anal. Calcd. for $C_{15}H_{11}O_3N$: C, 70.58; H, 5.14. Found: C, 70.62; H, 4.90.

Attempts to condense salicyl chloride with the amino-acetophenone in the presence of either alkali or pyridine were unsuccessful.

o-(*p*-Acetoxybenzoylamino)-acetophenone, $CH_3COOC_6H_4CONHC_6H_4COCH_3$.—To a vigorously shaken dispersion of 8 g. of *o*-amino-acetophenone in 200 cc. of 5% aqueous sodium hydroxide solution, there was added 20 g. of *p*-acetoxybenzoyl chloride, while the flask was cooled under tap water and the shaking was continued until the odor of the acid chloride had disappeared (long continued contact of the acetate so formed with excess of dilute caustic alkali solution gradually causes hydrolysis of this ester). The precipitate, when collected and dried, melted at 95°; yield, 15.2 g. or 89%. Recrystallized from alcohol to the constant melting-point of 97.5° (corr.), it formed colorless plates; yield, about 75%.

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.66; H, 5.09. Found: C, 68.60; H, 5.12.

Dilute aqueous solutions of caustic soda, hydrochloric or acetic acid, when warm, hydrolyzed both the ester and amide unions, giving *p*-hydroxybenzoic acid.

o-(*p*-Hydroxybenzoylamino)-acetophenone was obtained from the foregoing aceto derivative. The problem was to hydrolyze the ester grouping without simultaneous hydrolysis of the amide union, and two methods of accomplishing this were found. One was based upon the greater sensitiveness of the ester grouping to the continued action of cold dilute caustic alkali, and the other upon the greater stability of ethyl acetate.

In the former case, 15.2 g. of unrecrystallized acetate was shaken with 200 cc. of 5% sodium hydroxide solution until the solid was dissolved completely (three hours). Then the solution was acidified and the precipitate removed, dried and crystallized from 95% alcohol. Colorless needles were obtained, m. p. 219° (corr.); yield, 11.8 g. or 90%.

By the other method, 1 g. of the acetate was dissolved in 20 cc. of ethyl alcohol, 1 cc. of concd. sulfuric acid added, the solution warmed for 30 minutes at 50°, then diluted largely with water, the precipitate collected, dissolved in dilute caustic soda, the solution filtered from a small quantity of unhydrolyzed initial material, acidified, the precipitate removed and crystallized from alcohol; yield, 0.65 g.; m. p. 219° (corr.).

Of these two methods, the former proved the more satisfactory. This product could not be obtained by the method used for the isomeric salicyl derivative.

Anal. Calcd. for $C_{15}H_{11}O_4N$: C, 70.58; H, 5.14. Found: C, 70.04; H, 5.14.

All efforts to prepare the isomeric *o*-(*m*-hydroxybenzoylamino) derivative proved futile.

***o*-Nitrobenzoyl Isatinic Acid**, $O_2NC_6H_4CONHC_6H_4COCOOH$.—To a suspension of 11 g. of *o*-(*o*-nitrobenzoylamino)-acetophenone in 200 cc. of cold water, there was added a solution of 12.2 g. of potassium permanganate and 4 g. of potassium hydroxide in 100 cc. of water, and the mixture was allowed to stand at laboratory temperature for 48 hours with occasional stirring, the color gradually changing from the purple of the permanganate to the dirty green of the manganate. The manganese in solution was precipitated by the addition of 12 g. of ferrous sulfate dissolved in 100 cc. of water. The filtrate from the manganese oxides was acidified and the brownish nitrobenzoyl isatinic acid which separated was collected and dried; yield, 5 g. By repeated extraction of the manganese dioxide sludge with hot alcohol, 3.5 g. of the initial unoxidized acetophenone was recovered. Based upon the 7.5 g. of acetophenone actually oxidized, the yield of isatinic acid was approximately 60%. Because of the instability of these *o*-substituted isatinic acids, as found by Bogert and Nabenhauer,² further purification or analysis was not attempted. Hydrolyzed by caustic alkali, the compound formed isatin and *o*-nitrobenzoic acid.

Salicyl Isatinic Acid, $HOC_6H_4CONHC_6H_4COCOOH$.—To a solution of 2.5 g. of *o*-salicylamino-acetophenone in 10 cc. of 10% caustic soda solution, 40 g. of cracked ice was added and then a solution of 2.75 g. of potassium permanganate in 25 cc. of water. The color of the solution changed rapidly to green and, after standing for an hour at laboratory temperature, to a clear yellow. When it had stood for two hours longer at room temperature, the solution was removed from the dioxide sludge, acidified, the light-yellow precipitated isatinic acid collected, dissolved in 25 cc. of hot alcohol, the solution cooled and filtered from a small amount of unoxidized initial ketone, the filtrate heated to boiling and boiling water added carefully until the acid began to separate. As the solution cooled, the acid precipitated in yellowish, fluffy needles; yield, 2.5 g. or 90%. After several crystallizations, it melted with decomposition at about 209–210°, the melting point varying considerably with the rate of heating. Hydrolyzed by dilute sodium hydroxide solution, it yielded isatin and salicylic acid.

Anal. Calcd. for $C_{16}H_{11}O_5N$: C, 63.16; H, 3.86. Found: C, 64.28; H, 4.15.

These analytical figures indicate the difficulty experienced in the purification of the product.

***p*-Hydroxybenzoyl Isatinic Acid** was prepared in the same way as the analogous *o*-isomer, in similar yields and of approximately the same melting point. When hydrolyzed, it formed isatin and *p*-hydroxybenzoic acid.

Anal. Calcd. for $C_{16}H_{11}O_5N$: C, 63.16; H, 3.86. Found: C, 63.96; H, 3.93.

2-(*o*-Nitrophenyl)-quinazoline-4-carboxylic Acid, $O_2NC_6H_4C_8H_4N_2COOH$.—A solution of 5 g. of *o*-nitrobenzoyl isatinic acid and 7 g. of dry ammonia in 70 cc. of absolute methanol was heated in a sealed tube for ten hours at 140°, and the reaction product isolated as described beyond for the *o*-hydroxyphenyl derivative. After recrystallizing this crude product seven times from 50% alcohol, it melted at 235° (corr.) but was still impure, as shown by the following analysis.

Anal. Calcd. for $C_{18}H_9O_3N_3$: C, 61.01; H, 3.07. Found: C, 59.37; H, 3.64.

Not enough material was available for further purification, and the experiment was not repeated.

2-(*o*-Hydroxyphenyl)-quinazoline-4-carboxylic Acid, $HOC_6H_4C_8H_4N_2COOH$.—A solution of salicyl isatinic acid in absolute methanol, containing one to three g. of dry ammonia per g. of the isatinic acid, was heated in a sealed tube for 20 hours at 110°, after which the solvent was evaporated, the residue dissolved in hot water, the filtered solution decolorized and acidified carefully, and the yellow flocculent precipitate dried; yield, 99%. After five recrystallizations from dilute alcohol, the fine, yellow needles obtained melted constantly at 171° (corr.).

Anal. Calcd. for $C_{18}H_{10}O_2N_2$: C, 67.66; H, 3.79. Found: C, 67.84; H, 3.90.

ETHYL ESTER.—A solution of 1 g. of the acid in a little absolute alcohol was added to 20 cc. of absolute alcohol containing 5 g. of dry hydrogen chloride and after this solution had stood for 13 hours at laboratory temperature, it was heated for an hour and a half at 60° , then concentrated to small volume, about 50 cc. of water added, sodium carbonate added in excess and the cloudy suspension allowed to settle. The ester separated as a yellow solid; yield, 0.76 g. or 70%. After two recrystallizations from dilute alcohol it formed yellow, glistening plates, m. p. 115° (corr.).

Anal. Calcd. for $C_{17}H_{14}O_2N_2$: C, 69.37; H, 4.80. Found: C, 69.72; H, 4.89.

2-(*p*-Hydroxyphenyl)-quinazoline-4-carboxylic Acid, prepared in a similar manner from the corresponding isatinic acid and methanol solution of dry ammonia heated together in a sealed tube for 24 hours at 110° , was purified by crystallization from dilute acid until its melting point remained constant at 251° (corr.). It formed fine, yellow needles of somewhat more orange shade than its *o*-hydroxy isomer; yield, 95%.

ETHYL ESTER.—As only a small amount of the free acid was prepared, it was not analyzed but was all utilized for the production of its ethyl ester, by the method described above for its *o*-hydroxy isomer. After repeated crystallization from dilute acetone, it appeared in yellow plates, m. p. 159° (corr.); yield, 75%.

Anal. Calcd. for $C_{17}H_{14}O_2N_2$: C, 69.37; H, 4.80. Found: C, 69.11; H, 4.85.

2-Phenylquinazoline-4,2'-dicarboxylic Acid, $HOOC-C_6H_4-C_8H_4N_2-COOH$, was synthesized as described by Bogert and Nabenhauer.¹ Inasmuch as the pharmacological tests hitherto carried out had been with the di-ammonium salt, it was thought desirable to examine also the disodium salt, which was obtained as follows.

A saturated solution of 18.5 g. of the acid in hot absolute alcohol (760 cc.) was treated with a sodium ethylate solution prepared from 70 cc. of absolute alcohol and 2.65 g. of metallic sodium. The sodium salt separated rapidly as the solution was stirred. It was collected, washed with absolute alcohol until the washings were neutral to litmus, and it then formed fine colorless needles, easily soluble in water. The solution was neutral to phenolphthalein and to methyl orange and had a saline, slightly bitter taste. In the free flame it melted with decomposition and charring. Its pharmacological properties are now being studied by Professor Rockwood.

Summary

1. Various new acylated *o*-amino-acetophenones have been prepared.
2. These ketones have been oxidized to the corresponding isatinic acids.
3. From the isatinic acids, quinazoline derivatives of cinchophen type have been obtained and are being tested pharmacologically.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF THE MALLINCKRODT CHEMICAL WORKS]

REACTIONS OF ANESTHETIC ETHERS WITH POTASSIUM HYDROXIDE AND WITH MERCURY AND THE TEST FOR FOREIGN ODORS

BY EDWARD MALLINCKRODT, JR.

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Experience over a long period of years in the testing of ether has enabled us to interpret, with at least a fair degree of accuracy, the meaning of the various appearances that arise when ethers of different compositions and purity are tested for aldehyde with potassium hydroxide. In the hope of establishing a more complete understanding of this test, our conclusions and a few typical experiments are given in the following pages, together with some remarks on the action of mercury on ether containing peroxides and the results obtained by the application of the test for foreign odors to many cans of old anesthetic ether.

The U. S. Pharmacopœia (X edition) requires that no coloration shall develop within two hours when 10 cc. of ether is mixed with 1 cc. of potassium hydroxide test solution and occasionally shaken.

By breaking weighed, sealed glass bulbs of pure aldehyde under pure ether, three ethers were prepared containing, respectively, 0.025 g., 0.05 g. and 0.075 g. of aldehyde per 100 g. of ether.

By holding the test-tubes before a sheet of white paper, one observer detected a pale yellow color with ether containing 0.05% of aldehyde but could find no color with 0.02%. An observer making the test for the first time detected 0.1% of aldehyde but could detect no color with 0.05% after one hour. After several hours, however, he could detect the color. Another observer was able to detect 0.025% of aldehyde readily if care was used, but got no reaction with 0.0125%. A 5% potassium hydroxide solution was used as directed in U. S. P. VIII. Recently another trial has been made by entirely different observers using 5.6% potassium hydroxide (N) as directed by U. S. P. X. A solution of acetaldehyde in pure aldehyde-free ether was prepared and its aldehyde content accurately determined by titration. This solution was then diluted with pure aldehyde-free ether, making known aldehyde solutions of 0.005, 0.01, 0.02, 0.04 and 0.06% acetaldehyde. It was found that the temperature at which the test was made had quite a pronounced effect upon the minimum amount which could be detected. By holding the tubes in a good light, using a white paper background and comparing the color with a blank, using pure distilled water in the place of potassium hydroxide solution, and covering this with a layer of ether, the minimum amount which could be detected was 0.02% at 35°, while at 15° it required 0.04% to give a corresponding color. This places the maximum sensibility of the test under ideal conditions at 0.03%, making the observation at average laboratory temperature of 25°. It is safe to say that under average conditions the limit of sensibility of this test would be in the neighborhood of 0.05 to 0.06%.

This test appears to be much less sensitive than the test of the German and Austrian Pharmacopœias employing solid potassium hydrate. The use of solid potassium hydrate is to be preferred to the solution as a reagent for aldehyde, both on account of greater sensitiveness and because, as will

appear later, the various appearances around and on the surface of the lumps of potash give valuable indications as to the presence of alcohol and peroxides in the ether. We have never employed this test except to determine its sensitiveness in the above experiments.

The German Pharmacopœia (Ph. G. VI) requires that anesthetic ether (*aether pro narcosi*), when placed in a glass-stoppered bottle protected from the light, shall not become colored itself and shall not impart any color, after six hours, to freshly broken lumps of potassium hydroxide the size of a pea. Following the German procedure, 30 cc. of ether and 5 g. of fresh pure potassium hydroxide sticks were used in each test.

Baskerville¹ states that anhydrous ether should give no response in this test for twenty-four hours. It should be noted, however, that this reaction in the complete absence of water is not to be depended upon to indicate aldehyde, as the following experiments indicate.

Aldehyde Can Produce No Color in the Absence of Water

It was soon observed in applying this test to pure anhydrous ether containing 0.1% of pure acetaldehyde that the characteristic brown coloration tended to make its appearance on the curved surfaces of the fragments of potassium hydroxide sticks and not on the freshly broken surfaces. By sandpapering off the cylindrical surface, that surface lost its property of acquiring the brown color, behaving then like the freshly broken surfaces. By holding the sandpapered stick of potassium hydroxide in a steam jet for a few seconds and making the test with it, the coloration reappeared on the sandpapered surface, showing that the presence of a slight amount of moisture in the potash is necessary for the proper formation of the color.

It was thought that a trace of carbonate in the crust on the caustic sticks might be one of the causes of the coloration appearing on the cylindrical surfaces. Accordingly, a test was made using instead of potassium hydroxide, potassium carbonate containing about one and one-half molecules of water, and another test after drying the potassium carbonate at 120°. The ether used contained, besides traces of alcohol and water, sufficient aldehyde to color potassium hydroxide a good brown. After thirty-six hours under this ether, the potassium carbonate, both dried and undried, was uncolored. The ether was then poured from the potassium carbonate into bottles containing the usual 5g. portions of potassium hydroxide. The ether from the dried salt became strongly turbid at once and the pieces of potassium hydroxide after several hours acquired a pale yellowish-brown tint, whereas the ether from the undried potassium carbonate colored the potassium hydroxide a deep brown.

Evidently potassium carbonate, while it plays no part in the production of the color on the lumps of potassium hydroxide, is able to dry ether containing considerable aldehyde to the point where the potassium hydroxide test fails to indicate the presence of aldehyde by the production of the usual brown color.

Sensitiveness of the Solid Potassium Hydroxide Test

Pure anhydrous ether free of aldehyde was prepared and determinate amounts of pure aldehyde were added corresponding to 0.025 g., 0.05 g. and 0.075 g. per 100 g. of

¹ Baskerville and Hamor, *J. Ind. Eng. Chem.*, 3, 396 (1911).

ether. The best way to prepare such determinate solutions is by weighing pure aldehyde in small, sealed glass bulbs and breaking them under ether. Our solutions were prepared in this manner. Thirty cc. of these ethers were poured upon 5 g. of freshly-broken sticks of potassium hydroxide in glass-stoppered bottles. Duplicate bottles were made and placed in light-tight cases to test the effect of excluding the light as required in the above mentioned Pharmacopoeia. It was found necessary to reject the first set of tests, for there was so little moisture present that at the end of three hours the potash was still white, even in the ether containing 0.075 % of aldehyde. A large drop of water was now added to the bottle containing the ether with 0.075% of aldehyde and in twenty-five minutes the potash became distinctly brown, thus showing the remarkable part played by water in facilitating the reaction between aldehyde and alkali. Four fresh tests were prepared, one with the pure ether and three with the ether containing the aldehyde, and to each test was added one drop (about 0.04 cc.) of water. A set of four duplicates was placed in the dark. The ethers containing 0.075% and 0.05% of aldehyde began to show perceptible color in about fifteen minutes, the tests protected from the light showing a slightly deeper tint. At the end of two hours, the ether containing 0.02% of aldehyde had produced a good brown on the potash and the ether itself was a pale amber color. This sample was overlooked at the end of the first hour, but had it been observed, it is probable that the color could easily have been detected. However, the full depth of the brown does not appear until from two to four hours have elapsed and, with very small amounts of aldehyde, twelve hours may be required for maximum color. The pure ether used for making these solutions gave absolutely no reaction even after several days.² A comparison of the tests which had been protected from the light with those exposed to the ordinary daylight showed no marked difference. At the end of five hours, however, it was just possible to distinguish by their slightly darker tints the bottles which had been kept in the dark. It would seem that the importance of protecting the tests from light has been overestimated. We have observed some slight influence from light in other experiments, but we have not ascertained the exact nature of the effect. For extreme delicacy the exclusion of light is perhaps desirable.

Further experiments showed that this test will detect 0.01% of aldehyde in pure ether. The observer should familiarize himself with the indications of the test by comparing pure ether with ether containing known amounts of pure aldehyde. The test fails absolutely to give reliable indications at dilutions of 0.001% of aldehyde, although we made many attempts to increase its sensitiveness. Possibly some indications may be obtained with less than 0.01% of aldehyde, but below this limit we prefer to employ other reagents of greater sensitiveness. As will appear later, this sensitiveness (0.01%), representing the limit for pure aldehyde in pure ether, cannot be attained in applying this test to ordinary ethers unless the proper amount of water is present to overcome the interference produced by the alcohol normally present in such ethers.

The Significance of Turbidity and Effect of Alcohol

Baskerville and others appear to regard the appearance of a turbidity in the potassium hydroxide test as indicative of the presence of aldehyde.

"On covering 5 g. of solid potassium hydroxide in freshly broken pieces

² This degree of purity is not difficult to obtain by laboratory methods. Compare Wobbe, *Apoth. Ztg.*, 18, 466 (1903).

about 5 mm. in diameter with 30 cc. of the sample and allowing to stand for six hours tightly closed and protected from light and occasionally shaking, the potassium hydroxide should not acquire a yellowish color, no yellowish or brownish-colored substance should separate and *the ether should not become turbid or assume any color.*"³

The quotation appears ambiguous as to whether an ether which becomes turbid immediately and then clears up after several hours would be construed to have passed or to have failed. Presumably it would be held to have failed.

The absence of a turbidity, that is, the ether remaining water-clear in the potassium hydroxide test, seems to depend upon too many factors to be relied upon as a proof of the purity of ether. As the following tests indicate, the amount of alcohol present influences this largely, ethers rich in alcohol but perfectly pure and normal otherwise generally produce a turbidity which clears up more or less after several hours.

Twenty cubic centimeters of ether free from aldehyde and dehydrated over metallic sodium, to which had been added 0.72 cc. of absolute alcohol and 0.08 cc. of water to imitate the composition of anesthetic ether required by the U. S. Pharmacopœia (9th Edition now superseded by 10th), produced an immediate turbidity when poured upon the caustic. The aldehyde introduced by the alcohol is trifling. We have seen many specimens of ether of 0.711 sp. gr. (water and ether at 25°) which were sufficiently free from aldehyde to give to potassium hydroxide no color for eighteen hours and yet if several per cent. of "Cologne Spirits," which contains less aldehyde than the ordinary grain alcohol, were added to the ether, an immediate turbidity, when poured on the potash, would result.

To further demonstrate the influence of alcohol on the reaction, two aldehyde tests were made on a pure aldehyde-free ether containing about 3% of cologne spirits and to one of the test bottles two drops of water were added. After standing some twenty hours, the test without water was still slightly turbid and the potash showed a yellowish coloration, whereas the test containing water showed no turbidity and the potash remained white. It is evident that the turbidity and also the formation of a coloration which might easily be mistaken for a trace of aldehyde in the ether, is due to the alcohol. That the presence of alcohol interferes with the detection of aldehyde was known to Vulpus⁴ and confirmed by Schobig,⁵ who pointed out that ether containing several per cent. of alcohol dissolved 40 mg.⁶ of potassium hydroxide in 10 cc. and likewise tended to dissolve aldehyde resin, as shown by the yellow color of the ether.

We have repeated many times the experiment of adding several per cent. of cologne spirits to ethers in which the potassium hydroxide would remain almost, but not absolutely, snow-white for several days and always with the same general result, namely, more or less coloration at the end of about twenty-four hours upon the caustic and the production of a yellowish or brownish sediment. This deposit sometimes takes the form of

³ Ref. 1, p. 393.

⁴ Vulpus, *Apoth. Ztg.*, 9, 7 (1894).

⁵ Schobig, *ibid.*, 22, 210 (1894).

⁶ We found similar amounts dissolved by ether containing 4% of absolute alcohol.

feathery crystals several millimeters in length adhering to the lumps of potassium hydroxide. Whether or not one is prepared to admit the similarity between the shade of color produced by alcohol and that produced by aldehyde, the fact remains that alcohol greatly modifies the appearance of the test. The disturbance increases with increase in the amount of alcohol in the ether and the time of standing. When several per cent. of alcohol is present, twenty-four hours is too long to allow to stand before observation. Six hours is usually a safe time to allow for the aldehyde color to develop before the alcohol produces its yellow discoloration or feathery crystals, although tests will occasionally remain unharmed by the alcohol for twelve to eighteen hours.

We have stated that the presence of a certain amount of water in an ether containing several per cent. of alcohol helps to overcome the effect produced by alcohol in the potassium hydroxide test. In order to determine whether the sensitiveness of the test is diminished by the presence of water, and also the proper way to add the water, tests were made with fresh potassium hydroxide unexposed to moisture and with the same after it had stood overnight over water in a desiccator, and by a third procedure which consisted in adding a few drops of water to 30 cc. of the ether to be tested, shaking vigorously and then pouring the moistened ether over fresh potassium hydroxide. Four ethers of different composition were used, as follows.

Ether (1) was pure anhydrous ether containing 0.01% of aldehyde. It produced absolutely no color on unmoistened potassium hydroxide even for forty-eight hours, but the potassium hydroxide exposed to moist air showed a distinct brown in six hours. Ether (1) shaken with three drops of water did not produce as distinct a brown as the potassium hydroxide exposed to moist air, but it was still detectable.

Ether (2) was pure anhydrous ether containing 1.42% of absolute alcohol and was intended to show the disturbing effect of alcohol. With *unmoistened* potassium hydroxide, after six hours, this ether became turbid and yellowish and some precipitate formed, although the potassium hydroxide remained white. After twenty-four hours the color deepened and the potassium hydroxide appeared partially dissolved. Test valueless. In sharp contrast to the above, the *moistened* potassium hydroxide showed only a slight haziness after six hours. Ether (2) shaken with three drops of water remained clear for twenty-four hours and the potassium hydroxide was white except for a few minute, brownish crystals starting to form, indicating that the alcohol was beginning to show its effect.

Ether (3) was pure anhydrous ether containing 1.28% of absolute alcohol and 0.01% of aldehyde, and was designed to show the combined influence of alcohol and the least amount of aldehyde that can be detected by this test. With *unmoistened* potassium hydroxide, the ether was yellow after six hours, but the potassium hydroxide showed no true brown color. Test valueless. *Moistened* potassium hydroxide, however, after six hours, showed a faint true brown color, but after twenty-four hours the test was valueless, due to the effect of the alcohol. When ether (3) was shaken with three drops of water, the potassium hydroxide showed a trace of true brown after six hours, and after twenty-four hours the potassium hydroxide showed a distinct true brown and the test was still free from alcoholic effect.

Ether (4) was a pure anesthetic ether containing about 0.25% of water and 0.33% of alcohol to which 0.01% of aldehyde was added. This was intended to represent ordinary anesthetic ether such as might be met with on the market. It was of special interest, therefore, to show whether the potassium hydroxide test would detect the aldehyde in it. Both unmoistened and moistened potassium hydroxide showed a true brown in six hours. When ether (4) was shaken with three drops of water, the color after six hours' standing upon the potassium hydroxide was not so strong, but after twenty-four hours the color was practically normal.

Reaction of Mercury with Ether Containing Peroxides

Before considering certain abnormal indications which arise when the potassium hydroxide test is applied to ether containing peroxides, we will refer to the following chance observation made thirteen years ago.

Four or five samples of an excellent grade of anesthetic ether, originally free from aldehyde, which had been kept in glass-stoppered bottles for about a year in a laboratory closet (only occasionally exposed to daylight), were found to be rich in peroxides, but when tested for aldehyde in the usual manner with potassium hydroxide, produced only a slight brown color.

Copious precipitates, some black and some light gray, resulted on shaking these samples with mercury and the aldehyde test applied as above now quickly showed the characteristic dark brown color on the potash. One sample became almost black, indicating the presence of aldehyde far in excess of that generally present even in commercial ethers. No intensified reaction could be obtained by shaking with mercury an ether rich in aldehyde (containing over 0.1%) but free from peroxides and no reaction whatever could be obtained from pure ether by such shaking. The reaction is very sensitive and an ether which gives an easily recognizable yellow with cadmium potassium iodide will also show, when carefully observed, a slight tarnishing or production of a skin on the bright surface of a globule of clean mercury. Ether which has been in contact with rubber will blacken mercury, although containing no peroxides. The color of the precipitate due to peroxides is generally grayish-black but may be light gray or, if water is present, it may be yellowish.

Although the peroxides present in the ether were completely destroyed after five hours shaking with mercury on a vigorous mechanical shaker, the weight of the powder, because of its variable composition, even after allowing for the finely-divided metallic mercury in it, cannot be taken as a measure of the active oxygen present. We were forced to abandon the idea of a quantitative method based upon this reaction. The precipitate is non-explosive, contains considerable acetic acid and the color can be made to vary by digestion with water.

The use of mercury for removing traces of peroxides in ether is well known,⁷ but we have seen no reference to the simultaneous liberation of aldehyde. This reaction agrees with the results of Clover,⁸ who proved that acetaldehyde was one of the main decomposition products of the organic peroxides in many old ethers. Warming ether containing peroxides with a few drops of 50% sulfuric acid will often liberate sufficient aldehyde to indicate itself by the potassium hydroxide test.

⁷ Bein, "Ausdehnung des Aethyläthers, etc.," *Wissenschaftliche Abhandlung der Kaiserlichen Normal-Eichungs Kommission*, Heft VII, Metronom. Beiträge, p. 42.

⁸ Clover, *THIS JOURNAL*, 44, 1107 (1922).

Referring to the tarnishing of mercury by impure ether, Baskerville⁹ says "that only the presence of free sulfur or hydrogen sulfide can produce the reaction generally ascribed to organic sulfur, excepting, of course, hydrogen dioxide which produces a gray precipitate even when present in mere traces." It is true that mercury is very easily corroded even by 0.001% of the *organic* peroxides naturally occurring in ether, but by pure hydrogen dioxide it appears to be but little attacked, as the following experiments show.

To two portions of pure ether showing no reaction either with cadmium potassium iodide or ammoniacal silver nitrate, aqueous hydrogen peroxide was added equivalent to 0.01% of H_2O_2 and 0.1% of H_2O_2 , respectively. After shaking these two samples and also a comparison sample of pure ether for one hour with mercury, the mercury in the pure ether was only very slightly tarnished, the surface remaining bright except for a few separate specks; the ether containing 0.01% of H_2O_2 differed very slightly from the pure ether, the mercury containing a few more specks. The total tarnishing was insignificant in either. The ether containing 0.1% produced barely sufficient grayish powder to conceal the surface of the mercury, whereas ether containing 0.1% of the natural organic peroxides gives, as already stated, a copious precipitate. Other portions of each ether were allowed to stand for six days before shaking with mercury to test whether the mercury would then be greatly attacked, but the results were substantially the same. No hydrogen peroxide could be found in any of the samples after the shaking with mercury. Mercury is not very readily converted into the finely-divided metallic state by shaking with ether. After shaking the ether containing 0.1% of H_2O_2 with a weighed amount of mercury on a mechanical shaker for five hours, the loss of weight due to the formation of the powder which was separated from the globule before weighing amounted to less than 0.2 g. Another sample of ether containing 0.09% of H_2O_2 , when shaken for five hours with 2 cc. of mercury, produced a small amount of yellowish powder insufficient to cover its surface.¹⁰ After long contact with hydrogen peroxide, however, ether does acquire the property of readily corroding mercury, presumably because of the formation of organic peroxides as explained by Wieland and Wingler.¹¹

The Effect of the Presence of Peroxides

Baskerville⁹ states, as the result of his experiments, that "peroxides may cause a turbidity, but no coloration or colored separate." This is true, but this statement and the preceding paragraph should not be taken to mean that neither hydrogen peroxide nor the natural peroxides interferes with the detection of aldehyde by means of the potassium hydroxide test, as the following experiments indicate.

Ether containing about 0.15% of aldehyde was exposed to an ordinary glass mercury vapor light for sixty hours. A portion of the light-treated ether, which now gave a strong test for peroxides with the cadmium potassium iodide reagent, was shaken for five hours with metallic mercury to liberate the aldehyde. Comparative aldehyde tests

⁹ Ref. 1, p. 308.

¹⁰ The well-known catalysis of hydrogen peroxide by mercury (Bredig and Weinmayr, *Z. physik. Chem.*, **42**, 601 (1903)) would lead one to expect some such results with ether.

¹¹ Wieland and Wingler, *Ann.*, **431**, 301 (1923).

were next made using both fresh caustic and caustic exposed to moist air on the original ether, on the light-treated ether and on the latter after shaking with mercury. The caustic in the light-treated ether was almost white, showing less color than is produced by 0.01% of aldehyde, and there was only a slight increase even after twenty-four hours' standing. The portion of light-treated ether shaken with mercury produced in four hours a notably darker color estimated to be at least equal to the presence of 0.03% of aldehyde and the color increased considerably after twenty hours. With original ether, the aldehyde was evident in five minutes and after four hours the caustic was strongly colored rusty brown and considerably darker than the ether which was shaken with mercury. Evidently the liberation of the aldehyde is not quantitative. Sunlight produced similar results. Exposure to ordinary daylight for several hours seems to be without injurious influence, but a half day's exposure has produced the effect.

Aqueous hydrogen peroxide was added to ether containing 0.1% of aldehyde in the proportion of two molecules for one of aldehyde and the solution was kept in the dark for three days and occasionally shaken.¹² An aldehyde test now showed a scarcely perceptible yellow color after one-half hour. The color deepened somewhat on long standing but the caustic assumed a yellowish color and powdery appearance. A portion of the original ether treated with peroxide was shaken with mercury and the test then showed a strong reaction after twenty minutes, thus proving that the aldehyde was not destroyed. These experiments suggest a possible explanation for the fact frequently observed by us that ether rich in the naturally occurring peroxides gives only a feeble aldehyde reaction (or even none at all) with potassium hydroxide, although the ether when fresh may have contained sufficient aldehyde to give a dark brown coloration. It is clear that hydrogen dioxide and likewise the peroxide naturally occurring in ether interfere greatly with the production of the characteristic dark brown color, rendering the test far less sensitive and indeed practically useless for indicating small traces of aldehyde.

Potassium Hydroxide Test Applied to Peroxidized Ethers

Most specimens of ether containing several per cent. of alcohol will give, when they have acquired sufficient peroxide, a marked turbidity which persists for many hours and finally settles out as a yellowish or brownish precipitate after from eight to twelve hours. The lumps of potassium hydroxide then appear to have been pitted or partially dissolved and the test has a characteristic appearance.

In the case of peroxidized ether which originally contained little or no alcohol, no turbidity is produced, the ether remaining water-clear and the lumps of caustic frequently exhibit a sort of blistered appearance and are only slightly colored, due presumably to the liberation of a little aldehyde from the peroxides. The following examination is intended to illustrate these conclusions and gives the results obtained by applying the potassium hydroxide test to a number of samples of ether which had stood in amber bottles tightly stoppered with corks on the laboratory shelf for about six months, including the heat of the summer. The ether was originally of good quality, sp. gr. 0.711^{25°} and practically free from aldehyde, and to a portion of it several per cent. of pure cologne spirits had been added. Almost all of the bottles had partially evaporated, many having lost one-

¹² From Wieland and Winkler's work this result might be expected. Ref. 11.

quarter of their contents. For purposes of comparison, samples which were free of peroxides were also tested.

Of thirteen samples of alcoholic ether giving marked peroxide tests, all gave a *marked turbidity* when poured upon the potassium hydroxide. After about five hours' standing, six of the tests were still turbid, resembling a solution containing freshly precipitated aluminum hydrate. Four were yellowish and the precipitate had settled. Of six comparison samples (free of peroxides) five gave a slight turbidity upon pouring upon the potassium hydroxide, and after about five hours five were *slightly* turbid, but *none showed a marked turbidity* resembling aluminum hydrate. After standing overnight, eleven of the tests on the peroxidized ether were brownish and the potassium hydroxide lumps appeared partially dissolved, while five of the peroxide-free ethers showed only pale yellowish sediments and no dissolving of the potassium hydroxide. Of seventeen samples of the non-alcoholic ether giving marked peroxide reactions, four showed a turbidity after the test had stood for five hours, the balance being clear; but in eleven of these the potassium hydroxide was yellowish and in eight the potassium hydroxide had a blistered appearance in addition to being colored. Four comparison samples (peroxide free) were all clear and the potassium hydroxide white in three and almost white in the fourth.

Anyone using the test with solid potassium hydroxide day in and day out on ethers of varying composition will be struck by the variations in the phenomena attending the test, and herein lies its chief defect, for the observer must make allowances for the disturbing influences caused by the presence in the ether of such common impurities as alcohol and peroxides. The pure brown coloration on the lumps of potash normally produced by pure aldehyde in pure ether may be obscured or replaced more or less by the other appearances which, while difficult to describe in an adequate manner, are readily recognized after having once been seen.

We may sum up briefly the results of all experiments with the potassium hydroxide test as ordinarily employed, using lumps of potash, as follows.

As a means of detecting aldehyde it is unreliable in the presence of peroxides unless these are present only in very small traces. Before applying the test, such ether may be shaken with mercury to liberate the aldehyde combined with the organic peroxides. However, what evidence we have indicates that this decomposition is not quantitative.

The appearance of a turbidity which remains undiminished in intensity for some hours points to an alcoholic ether containing considerable peroxides. Alcohol itself produces a turbidity which is not easy to distinguish from that due to peroxides. Contrary to the prevailing opinion, the appearance of a turbidity is in no way indicative of the presence of aldehyde and is an indication from which no positive conclusions can be drawn unless substantiated by other tests.

The test will not indicate aldehyde in the complete absence of water. The presence of several per cent. of alcohol in ether, especially if not accompanied by the usual amount of water, produces a coloration which resembles the aldehyde color. The use of potassium hydroxide which has

been exposed to moist air will avoid the first difficulty, but to avoid the second it may be necessary to moisten the ether with water, three drops to 20 cc. If this is done, the effect of the alcohol which otherwise may manifest itself in several different appearances on the lumps of caustic is delayed for at least twelve to eighteen hours, amply sufficient to allow the aldehyde color to attain its maximum. While it is easy to detect 0.01% of aldehyde in pure ether, it requires some experience and the proper use of water to detect this amount in an alcoholic ether. Since many anesthetic ethers contain from 0.5 to 1% of water,¹³ the use of potassium hydroxide exposed to moist air will suffice if fresh caustic fails to indicate aldehyde, but in the absence of any information concerning a given specimen three tests should be made: namely, with fresh caustic, with caustic which has been exposed to moist air and by using water in the ether itself.

When ether contains both alcohol, to the extent of several per cent., and considerable aldehyde, say 0.1%, there is generally formed a precipitate which resembles ferric hydrate both in form and color.

We have occasionally noticed a transient yellow color which appeared on the potassium hydroxide in some of the tests and then disappeared at the end of about twelve hours. This was finally traced to test bottles which were rinsed with alcohol, then with ether, and the caustic put in before the bottles were fully dry. Various kinds of potassium hydroxide were investigated before the cause of the color was discovered and it may be remarked that the test is not much influenced by the purity of the alkali. Obviously, however, the pure white sticks are the best to use in this test.

Acrolein and furfural, if added in small quantities to ether, impart a color to potash similar to the aldehyde color. Paraldehyde in traces produces no color in this test unless the ether containing it is previously warmed with a drop of sulfuric acid, which suffices to liberate the aldehyde. These substances, however, are not known to occur in ethers of modern manufacture. A more likely source of trouble lies in the use of ordinary corks for, as pointed out by Baskerville,³ ether may dissolve substances from cork which cause the potash to discolor in the absence of aldehyde.

Test for Foreign Odors

The usual practice is to evaporate slowly on a steam-bath, without rapid boiling, 30 cc. of the ether to be tested in a small beaker covered with a watch glass. When the ether has evaporated to a residue of one or two cubic centimeters, the residue is poured drop by drop on the center of a clean piece of filter paper; four inches square is a convenient size. The evaporation keeps up with the dropping and a spot about the size of a half dollar is formed. Practice enables one to judge when the ether has almost disappeared and at this instant the wet spot, which now contains the

¹³ Mallinckrodt and Alt, *J. Ind. Eng. Chem.*, 8, 807 (1916).

substances less volatile than ether, should be placed close to the nostrils and smelled. With pure ether containing little or no odor, the damp spot at the center of the paper may be laid over the nostrils and air drawn into the nose. This test is so sensitive that an aroma different from the smell of ether itself may be detected with nearly every ether, no matter how prepared, and good judgment should be used in interpreting the results. The value of such a sensitive test lies in concentrating any traces of irritating substances present in the ether, which are masked more or less by the smell of the ether itself, and presenting them to the nostrils in such a way that their pungency or irritating effect cannot be mistaken. The appearance of the spot is very characteristic and should be carefully noted. The presence of several per cent. of alcohol may be detected by the appearance and smell of the spot. Water shows plainly by the slowness with which the spot evaporates from the paper. One drop of acetic or formic acid or one drop of oil of wine in 30 cc. of ether is easily recognized. Frequently the spot at the center of the paper on which the ether has been poured shows an oily appearance, or an oily margin about the circumference of the spot. This occurs in the case of ethers containing peroxides, due to the concentration of the latter being only slightly volatile. When such a spot is placed to the nostrils and air drawn into the nose, a very characteristic irritating odor, somewhat like pepper, is noticed which, after a few moments, becomes still more irritating to the lining of the nostrils. If a few drops of the cadmium potassium iodide reagent, as used for the peroxide test, is applied to the oily line, iodine is immediately liberated and stains the paper brown or bluish. The pure oil, on the other hand, rich in organic peroxides,¹⁴ which we obtained by fractionation of old ether, had of itself very little odor, but if several drops are added to 30 cc. of pure ether and the odor test applied, the characteristic irritating odor of peroxidized ether appears.¹⁵

The odor test is of little value for detecting volatile impurities which distil with the ether vapor itself. Fortunately there are none such likely to occur in ether. A few drops of aqueous sulfurous acid in 30 cc. of ether could neither be detected by the odor test nor could it be detected by pouring the ether directly on filter paper and smelling.

In one experiment, sixty-five sealed cans of ether, averaging about one year old and ranging from about seven months to a year and a half, were found to contain fifteen cans which had pronounced bad odors. Of the fifteen bad cans, nine gave pronounced reactions for peroxides and each of the nine, when subjected to the odor test, gave the pungent, peppery

¹⁴ Clover (Ref. 8, p. 1112), on the other hand, found that his pure "ether peroxide" had an irritating odor.

¹⁵ This interesting fact was noted by Dr. W. N. Stull in our Laboratory fifteen years ago and has been confirmed by later experience.

odor characteristic of peroxides. There were only two cans in the lot which gave affirmative test for peroxides which failed to give the characteristic odor, but these cans showed only a very slight reaction with the cadmium potassium iodide reagent. The close relation between the presence of peroxides and a certain kind of odor is evident.

Summary

1. Under average conditions, if ether contains less than about 0.05% of aldehyde it will probably not be detected by the official aldehyde test in U.S.P. X, whereas the test employing solid potassium hydroxide will, by employing the precautions given in this paper, detect 0.01%.

2. Peroxides and alcohol, if present in the ether, produce characteristic appearances in this test and their effects are described.

3. Shaking with metallic mercury provides a convenient means of decomposing the organic peroxides naturally occurring in old ether with liberation of acetaldehyde in accordance with the work of Clover and of Wieland and Winger on the constitution of these peroxides.

4. The presence of more than minute traces of peroxides in ether can be detected by a characteristic odor when the ether is evaporated to small volume and smelled after pouring upon paper.

ST. LOUIS, MISSOURI

NOTE

Reduction of Benzophenone by Magnesium Amalgam. Correction.—In a recent paper¹ we reported that magnesium amalgam did not reduce benzophenone, contrary to statements of others.² Because of the positive results obtained in the case of benzil³ with magnesium amalgam, the experiments on benzophenone were repeated. We again experienced the same difficulty as before with amalgam that had been prepared as previously by heating together magnesium and mercury. However, in several instances of a number of experiments it was observed that a simple mixture of magnesium metal and mercury at room temperature effected reduction of benzophenone. We are at present at a loss to explain the differences in the results obtained.

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¹ Gomberg and Bachmann, *THIS JOURNAL*, 49, 236 (1927).

² Schlenk and Thal, *Ber.*, 46, 2847 (1913).

³ Gomberg and Bachmann, *THIS JOURNAL*, 49, 2584 (1927).

NEW BOOKS

Periodic Table. Reprinted and enlarged from General Chemistry by HORACE G. DEMING. 95 X 155 cm. John Wiley and Sons, Inc., 440 Fourth Avenue, New York. Price, \$3.50.

In general principle this chart is similar to one in Nernst's Theoretical Chemistry and still more closely related to the chart of Antropoff, reviewed in *THIS JOURNAL*, 49, 888 (1927). While it does not have the colors of the Antropoff chart, the same relations are brought out by connecting lines. It contains a number of valuable features not found in the other chart, especially the successive shells of electrons for the inert gases and the radioactive disintegration relations. The chart will be very useful for recitation rooms and offices.

WILLIAM A. NOYES

Theorie der Adsorption von Gasen (Theory of Gas Adsorption). By EMANUEL JAQUET. Gebrüder Borntraeger, W 35 Schöneberger Ufer 12a, Berlin, 1925. 56 pp. 17 figs. 25.5 X 16.5 cm. Price, unbound, 4.80 M.

The theory of adsorption is developed by considering the adsorbed molecules as systems of electric charges (dipoles or quadrupoles) in thermal equilibrium in a variable electric field due to the contiguity of an adsorbing surface, regarded as a perfect conductor or dielectric. First, the form of the isotherm is investigated, and several methods are suggested for allowing for the intermolecular action which causes departures from Henry's law. The equation best fitting the experiments is one which is essentially the same as that given by Langmuir,¹ although the author does not mention this. Next, a method is derived for estimating the maximum adsorption energy from the observed temperature coefficient of the initial slopes of the isotherms, having regard to the fact that at high temperatures the adsorbed molecules do not occupy positions of minimum potential energy, so that the mean energy, as given by the temperature coefficient, must be multiplied by a factor. Expressions for the electrostatic energy of dipoles and quadrupoles in the vicinity of a conducting wall are derived, and found to involve the molecular diameter, the electrical moment or moment of inertia and, to a secondary degree, the polarization constant. In the case of dipoles, the energy should show a marked temperature variation owing to changes in molecular orientation.

The conclusions are tested by comparison with experiment, and tolerably verified, the values of the constants obtained being of the same order of magnitude as those derived by other means.

A. S. COOLIDGE

¹ Langmuir, *THIS JOURNAL*, 38, 2268 (1916), eq. (16).

A Text-Book of Organic Chemistry. By Dr. JULIUS SCHMIDT, Professor of Chemistry in the Technical High School, Stuttgart. English Edition by H. GORDON RULE, Ph.D., D.Sc., Lecturer in Organic Chemistry, University of Edinburgh. D. Van Nostrand Company, 8 Warren Street, New York City, 1926. xxiv + 798 pp. 24.5 × 17 cm. Price \$9.00.

The author intended to write "a book which stimulates the reader to think for himself." There is every reason to believe that he has been successful in this endeavor. This text is remarkably free from errors in spelling and in punctuation. On page 143, footnote numbers are omitted. This is all the more evident because of the notable freedom from such slips in the book as a whole. In general, the print work indicates that the book has been carefully made up and proof-read. It is characterized by an abundance of references to the original literature.

The material included in the first part of the volume is too elementary for the remainder of the work. It is, for example, useless to indicate the mode of calculating empirical formulas in a book which subsequently deals at some length with such a subject as osotriazoles. No endeavor is made to avoid the use of such terms as normal and iso before these are explained. It is, at least, debatable whether or not the book might not really benefit by the elimination of all material on analyses, and thus do away with the first sixteen pages. This specialized branch of organic chemistry might preferably be covered in a separate volume.

The statements in this book are concise and clear, and characterized by a feature almost unique, namely, the designation of the specific reagents utilized in various reactions, instead of the all too common and very unsatisfactory remarks to the effect that this or that change is produced by oxidation, reduction, etc., found in so many other books. It is pleasing to note the translator's conformity with the rules for numbering organic ring systems, recently published by a Committee of the International Union of Pure and Applied Chemistry.

In the discussion of the determination of molecular weights by the Victor Meyer method, references to air as a standard are superfluous and simply make the computations unnecessarily involved. Certain of the statements dealing with 1,4 addition are surprising, especially when consideration is given to the well-known work on conjugated systems in alpha, beta unsaturated ketones with the Grignard reagent. In the description of melting-point determinations, there is altogether too much detail, quite unnecessary if it is assumed that the reader is capable of appreciating most of the material in the book.

The slowness with which facts in the periodical literature get into texts is nowhere more evident than in the neglect to correct the hoary statement that $C_{60}H_{122}$ is the highest known member of the saturated hydrocarbon series; this despite Gascard's publication dealing with $C_{64}H_{130}$, which ap-

peared in 1921. The residents of Seminole County, Oklahoma, might be excused some righteous indignation if they took violent exception to the statement that Pennsylvania is the most important source of petroleum in North America.

Occasionally the rather loose use of the term "solution" instead of the more exact "colloidal suspension" may be noted. In the description of the purification of crude ether, the recommendation that quicklime be used to remove alcohol hardly seems reasonable. The designation of certain compounds as isonitriles might advantageously be changed to isocyanides. The more desirable pinacol and pinacolone for pinacone and pinacolone have not been utilized. In dealing with the formation of glycol chlorohydrin, the use of hypochlorous acid and ethylene is not mentioned. Sufficient years have elapsed since the World War so that this process, of no mean importance, might be expected to be found in a book of such scope as this. Almost invariably textbooks indicate that dynamite is made of kieselguhr, whereas generally, and certainly uniformly in the United States, wood pulp or wood powder is used.

In the section on monosaccharides, these compounds are classed according to the number of carbons in the molecule without reference to the modern tendency to use the number of oxygens instead. When this method is used, rhamnose and similar compounds are, quite as a matter of course, regarded as pentoses, which is in accordance with their chemical behavior. The formula for lactose is incorrect, but it is too much to expect anything else. The formula most recently suggested by Haworth, wherein both parts have amylenoxide rings and the bioc attachment is on carbon 4 in the glucose part, is, however, more acceptable than that given. The formulas for the uric acid syntheses in one case indicate potassium cyanate, whereas cyanic acid would be in accord with what is subsequently given. In naming saturated alicyclic compounds, both the polymethylene and the more preferable cyclo systems are employed. In one instance, both designations appear in the same sentence. In the conversions of aromatic to aliphatic compounds, no mention is made of the very important industrial preparation of maleic anhydride by the catalytic oxidation of benzene. In the portion dealing with furane derivatives, instead of the more desirable furane, furfuran designations are employed. It would seem advantageous to indicate the possibility of the furfuran scheme, and thereafter to employ consistently the more modern furane naming.

In the section on proteins, it is stated that "most of it (nitrogen) is present in peptide groups." This is certainly debatable in the light of recent information concerning the possible occurrence of dioxopiperazines, pyrrole and even ureide complexes in this extraordinarily important group of substances. It is, of course, impossible to have any text absolutely up-to-date in all matters, and this is doubly true of a translation, but it

seems that an inkling of something other than the classical peptide structure for proteins might have been included. Certainly that "it may be stated with confidence that most of the constituent parts of proteins have now been identified" requires clarification, at least to the extent of the author's meaning of the term "constituent parts." It must be admitted that a dioxopiperazine derivative is mentioned as a protein degradation product, but not in such a manner that even by intimation can one conclude that dioxopiperazines may be present as such in the protein molecules.

The special sections on the various classes of ring compounds are unusually numerous and seem to have been especially well treated.

It has been stated that it is an American characteristic never to praise anything without immediately qualifying the approval. In this instance the procedure will be reversed. Despite the criticisms of this volume, it should be recognized as one of the most stimulating, lucid and useful of the larger organic chemistry texts, and an eminently worth while production.

G. ALBERT HILL

Textbook of Biological Chemistry. By JAMES SUMNER, Ph.D., Assistant Professor of Biological Chemistry, Cornell University. The Macmillan Company, 60 Fifth Avenue, New York City, 1927. xxiii + 283 pp. 6 figs. 22.5 × 14.5 cm. Price \$3.50.

Five chapters on the subjects of fats, carbohydrates, proteins, urine and blood make up about two-thirds of this book. The chemistry of digestion is treated in short sections under the chapters on fats, carbohydrates and proteins. The chemistry of muscle, nerve and bone is almost entirely neglected as is also that of the mineral constituents of the tissues. The book is intended for elementary students and, presumably for that reason, no references are cited. The somewhat frequent use of workers' names is hardly in line with the same principle. Typographical errors occur on pages xxii and 91. The names Macleod and Schafer are misspelt on page 68.

GEORGE HUNTER

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PRIMARY DECOMPOSITION OF MOLECULES IN PHOTOCHEMICAL REACTIONS

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Introduction

Excited atoms and molecules produced by the primary action of the absorbed light have been found to be effective in stimulating photochemical changes in a number of photochemical reactions. When excited atoms or molecules are produced by the absorption of light, the absorption spectrum of the gas consists of lines or bands, respectively.

Recently it has been found that not all absorbers in photochemical reactions have line or band spectra. In fact some exhibit continuous absorption. Some writers have concluded that if the absorption spectrum of a diatomic molecule is truly continuous, the molecule is disrupted or decomposed into atoms when the frequency of the absorbed radiation is not great enough to produce ionization. Those photochemical reactions in which the absorber molecule has a continuous spectrum in the region of the spectrum under investigation, and consequently those in which the primary action of the light decomposes the molecule into atoms, have been called primary decomposition photochemical reactions in contrast to the excited atom or molecule types.

It is pointed out in this paper that a given photochemical reaction may belong to the excited molecule type in one region of the spectrum and to the primary decomposition type in another region of the spectrum; also that the quantum efficiency of the primary decomposition type is independent of the wave length and pressure, whereas it is not independent in the excited atom or molecule types.

Historical

Einstein's Law of Photochemical Equivalence, when tested by comparing the number of molecules which react with the quanta of radiation

absorbed, appears to have been violated¹ in the majority of reactions which have been quantitatively studied. In the abnormally low yields the absorbed light energy may lose its effectiveness by fluorescence or ineffective collisions. Abnormally high yields may be attributed to chain reactions. While secondary reactions are of fundamental importance, it is wished to restrict the discussion primarily to the primary action of the light.

It is now accepted as fact that band spectra are attributed to change in rotational or vibrational or electronic energy levels or a combination of these changes in the molecules. On this basis Stern and Volmer² have taken issue with Warburg's³ assumption that gaseous hydrogen bromide and hydrogen iodide are decomposed into atoms as a primary action of ultraviolet light. Moreover, they suggested that the hydrogen halide molecule is first excited by the ultraviolet light and that a collision of the excited molecule with a normal molecule produces a hydrogen and a halide molecule. More recently Franck⁴ and Bodenstein¹ have also postulated that in general the primary action of light in photochemical reactions produces an excited molecule. Mulliken⁵ assumed that iodine vapor in the visible spectrum is dissociated into atoms by the absorption of light in a region of continuous absorption. The reason given for this assumption is that in its absorption spectrum the vibration frequency of the atoms in the molecule approaches zero and that the band absorption spectrum in this region of the spectrum merges into a region of continuous absorption. In addition Franck⁴ and Dymond⁶ have observed that the absorption of light by the iodine molecule in the region of continuous absorption produces no fluorescence. With this additional evidence, Franck⁴ asserts that the halogens are dissociated into atoms by the absorption of light in the region of continuous absorption. He also states that one of the dissociated atoms must be excited, inasmuch as the threshold value for the spectroscopic energy of dissociation is greater than the thermochemical value. Birge⁷ and his associates have found that the absorption spectrum of oxygen is similar to that of iodine. In addition they have been able to calculate heats of dissociation of molecules from vibrational energy terms of band spectra data.

Tingey and Gerke⁸ have made observations on the ultraviolet absorption spectra of hydrogen bromide and hydrogen iodide during photochemical

¹ Bodenstein, *Trans. Faraday Soc.*, **21**, Part 3 (1925).

² Stern and Volmer, *Z. Wiss. Phot.*, **19**, 275 (1920).

³ Warburg, *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

⁴ Franck, *Trans. Faraday Soc.*, **21**, Part 3 (1925).

⁵ Mulliken, *Phys. Rev.*, **25**, 509 (1925).

⁶ Dymond, *Z. Physik*, **34**, 553 (1925).

⁷ Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

⁸ Tingey and Gerke, *THIS JOURNAL*, **48**, 1836 (1926).

decomposition. These spectra were found to be continuous. It was concluded that these molecules were dissociated into atoms by the primary action of the light.

Additional examples of photochemical reactions will be found in Table I, in which the absorption spectra indicate that the primary action of the light is the dissociation of the molecules. Examples of the excited molecule class for which the spectroscopic data exist also will be listed in Table I.

The first class listed in Table I is called the "excited reactant" class, in which molecules are excited by the primary action of light absorption. Then by a collision the excited reactant molecule produces a photochemical reaction. The second class is called the "excited sensitizer" class, in which the radiation is absorbed by the sensitizer or catalyzer. This excited sensitizer then by a collision with the reactants utilizes this absorbed energy in producing photochemical change between reactants. The third class listed in Table I is called the "primary decomposition" class, in which the primary action of the absorbed light by the reactant is to produce decomposition of the reactant or sensitizer. It is stated whether great care was taken to remove traces of moisture. In those reactions in which heat is absorbed, the photochemical efficiency is usually low. In the exothermal reactions it is possible that the photochemical efficiency may become very great, especially in those reactions where traces of water are present. In this table it is noticed that there are very few exothermal reactions which are listed as reactions with secondary spontaneous chain reactions. This is due to the absence of data on the photochemical efficiency of these reactions in which water has been excluded.

TABLE I
PHOTOCHEMICAL REACTIONS

Reaction	Absorbing reactant or sensitizer	Type of abs. spectrum	Wave length of active radiation, Å	No. of quanta of radiation abs. per mol. of reactant	Sign of heat effect of Col. 1 reaction
Excited reactant					
$O_2 = \frac{1}{2}O_2^{*10,11,12}$	O_2	Band ¹²	1970-1756 ^{13,14}	1 04-3 42 ¹¹	Endothermic
$NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2^{15}$	NH_3	Band ¹⁴	2260-1515 ^{14,16}	2-10 ^{15,17}	Endothermic
$O_3 = \frac{1}{2}O_2^{18}$	O_3	Band	6700 ¹⁸ and U v ¹⁹	Exothermic
$H_2 + \frac{1}{2}O_2 = H_2O$ (dry) ¹²	O_2	Band	1970-1756 ¹⁴	Exothermic
$CO + \frac{1}{2}O_2 = CO_2$ (dry)	O_2	Band	1970-1756 ¹⁴	Exothermic

⁹ Lenard, *Ann. Physik*, **1**, 480 (1900).

¹⁰ Goldstein, *Ber.*, **36**, 3042 (1913).

¹¹ Warburg, *Sitzb. preuss. Akad. Wiss.*, 216 (1912); 644 (1913); 872 (1914).

¹² Tram, *Z. physik. Chem.*, **105**, 356 (1923).

¹³ Kayser, "Handbuch der Spectroscopie," **3**, 360 (1905).

¹⁴ Leifson, *Astrophys. J.*, **43**, 73 (1926).

¹⁵ Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911); 216 (1912).

¹⁶ Ferriers, *Compt. rend.*, **178**, 202 (1924).

¹⁷ Kuhn, *ibid.*, 177, 956 (1923).

¹⁸ Griffith and Shutt, *J. Chem. Soc.*, **119**, 1948 (1921).

¹⁹ Fabry, *J. Math. Phys.*, **4**, 1 (1925).

TABLE I (Concluded)

Reaction	Absorbing reactant or sensitizer	Type of abs. spectrum	Wave length of active radiation, Å.	No. of quanta of radiation abs. per mol. of reactant	Sign of heat effect of Col. 1 reaction
$\text{CH}_3\text{COH} + \frac{1}{2}\text{O}_2 = \text{CH}_3\text{COOH}^{20}$	CH_3COH	Band	2800-2350 ²⁰	Exothermic
Excited sensitizer					
$\text{H}_2 = 2\text{H}^{21}$	Hg	Line	2536	Endothermic
$\text{O}_2 = \frac{1}{2}\text{O}_2^{22}$	Hg	Line	2536	Exothermic
$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}^{23}$	Hg	Line	2536	Exothermic
$\text{N}_2\text{O} = \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2^{24}$	$\text{NO}_2\text{-N}_2\text{O}_4^{24}$	Band ²⁵	4600-4000 ²⁴	Very small
$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{N}_2 = \text{NH}_3^{26,27}$	Hg	Line	2536	Exothermic
$\text{H}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6^{27}$	Hg	Line	2536	Exothermic
$\text{H}_2 + \text{CO} = \text{HCOH}^{27}$	Hg	Line	2536	Very small
$\text{H}_2 + \text{CO}_2 = \text{H}_2 + \text{CO}_2^{27}$	Hg	Line	2536	Endothermic
$\text{O}_2 = \frac{1}{2}\text{O}_2^{28}$	Hg	Line	2536	Endothermic
Primary decomposition					
$\text{HCl} = \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$ (dry) ²⁹	HCl	Cont. ¹⁴	2640-1800 ⁸	
$\text{HBr} = \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Br}_2$ (dry) ^{30,31}	HBr	Cont. ⁸	3320-1800 ⁸	0.521-0.502	Endothermic
$\text{HI} = \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$ (dry) ^{29,32,33}	HI	Cont. ⁸	2600-1800 ²⁹	0.526-0.495	Endothermic
$\text{H}_2\text{S} = \text{H}_2 + \frac{1}{2}\text{S}_2$ (dry) ^{30,31,33}	H_2S	Cont. ²⁹	2300-1800 ²⁹	Very small
$\text{CH}_3\text{COH} = \text{CH}_4 + \text{CO}^{30}$	CH_3COH	Cont. ²⁹	2300-1800 ²⁹	Endothermic
$\text{I}_2 = \text{I} + \text{I}_{(\text{ex})}^{34,35}$	I_2	Cont. ^{4,6,25}	5000 ^{4,6,25}	Endothermic
$\text{Br}_2 = \text{Br} + \text{Br}_{(\text{ex})}^{36}$	Br_2	Cont. ^{4,25}	5200 ²⁵	Endothermic
$\text{Cl}_2 = \text{Cl} + \text{Cl}_{(\text{ex})}^{37}$	Cl_2	Cont. ^{4,25,28}	4800 ^{25,28}	Endothermic
$\text{Cl}_2 + \text{H}_2 = 2\text{HCl}$ (dry) ^{22,34,35}	Cl_2	Cont.	3000 ²²	chain ²⁵	Exothermic
$\text{Cl}_2 + \text{CO} = \text{COCl}_2$ (dry) ³⁵	Cl_2	Cont.	Ultraviolet ¹²	Exothermic
$\text{Cl}_2 + \text{SO}_2 = \text{SO}_2\text{Cl}_2$ (dry) ³⁵	Cl_2	Cont.	Ultraviolet ¹²	Exothermic
$\text{O}_2 = 2\text{O}^{38}$	O_2	Cont.	1750 ¹⁴	Endothermic
$\text{O}_2 = \frac{1}{2}\text{O}_2^{39}$	O_2	Cont.	1750 ^{26,34}	Endothermic
$\text{O}_2 = \frac{1}{2}\text{O}_2^{37}$	$\text{O}_2\text{-Cl}_2$	Cont.	4300 and 4060 ³⁷	0.54-0.43 ³⁷	Exothermic
$\text{O}_2 = \frac{1}{2}\text{O}_2^{37}$	$\text{O}_2\text{-Br}_2$	Cont.	4360 and 4060 ³⁷	0.035-0.029 ³⁷	Exothermic

It is possible to have a complex reaction in which the rate of the reaction is the sum of the separate rates which correspond to the classes listed above. Thus in Table I the decomposition of ozone in the presence of chlorine

²⁰ Henri, "Structure des Molecules," J. Hermann, Librairie Scientifique, 6, Rue de la Sorbonne, Paris, 1925, p. 100.

²¹ Franck and Cario, *Z. Physik*, **11**, 161 (1924).

²² Weigert, *Z. physik. Chem.*, **106**, 407 (1923).

²³ Marshall, *J. Phys. Chem.*, **30**, 34 (1926).

²⁴ Daniels and Johnston, *THIS JOURNAL*, **43**, 72 (1921).

²⁵ Wood, "Physical Optics," The Macmillan Company, New York, 1923.

²⁶ Noyes, *THIS JOURNAL*, **47**, 1003 (1925).

²⁷ Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

²⁸ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

²⁹ Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

³⁰ Bertholet and Gaudechon, *Compt. rend.*, **150**, 1517 (1910).

³¹ Smits and Aten, *Z. Elektrochem.*, **16**, 264 (1910).

³² Teves, Unpublished.

³³ Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

³⁴ Cohn, *Ber.*, **56**, 696 (1923).

³⁵ Marshall, *J. Phys. Chem.*, **29**, 1453 (1925).

³⁶ Born and Gerlach, *Z. Physik*, **5**, 433 (1921).

³⁷ Bonhöffer, *ibid.*, **13**, 94 (1923).

as a sensitizer is the sum of the rate of decomposition of ozone caused by its own absorption of light and the rate of decomposition caused by the absorption of light by the catalyzer, chlorine. The decomposition of ozone in the presence of chlorine or bromine, as listed in Table I, is principally sensitization by primary decomposition. When more reactions of this type are investigated, it may be convenient to subdivide primary decomposition photochemical reactions into the reactant and sensitizer classes.³⁸

Einstein's Law of Photochemical Equivalence

Einstein's law of photochemical equivalence appears to have been found wanting in all of the "excited reactant" and "excited sensitizer" photochemical reactions in Table I. The reason which has been given for the failure of this law lies in the possibility that the excited reactant or sensitizer may re-radiate the absorbed radiation as fluorescent radiation or lose it by collisions which are ineffective in producing photochemical reactions. (On the other hand the examples of the "primary decomposition" class in Table I which have been quantitatively investigated are in complete harmony with Einstein's law. The photolyses of hydrogen bromide and hydrogen iodide have been quantitatively investigated as a function of temperature, wave length, pressure, inert gas and in the liquid state with the universal result that two molecules are decomposed per quantum of absorbed radiation.^{1,39}

While the data are very complete for these two reactions, data on other reactions should be available before it would be certain that only "primary decomposition" photochemical reactions obey Einstein's law. Moreover, it would seem reasonable that every quantum of absorbed light which decomposes a molecule into atoms has a better chance of producing secondary reactions than one which produces an excited molecule in which one of the electrons is temporarily lifted to a higher energy level.

The Halogens.—In the band absorption spectra of the halogens the vibration frequency approaches zero and a region of continuous absorption sets in. Mulliken⁶ has assumed that it was possible that the halogens were decomposed into atoms in the region of continuous absorption. Franck⁴ and Dymond⁶ have assumed that the halogens are decomposed into a normal atom and an excited atom because the radiant energy is greater than the thermochemical heat of decomposition. They also state that the iodine fluorescence cannot be excited by absorption of the light

³⁸ The writer is indebted to Professor S. C. Lind for this suggestion.

³⁹ It is not to be expected that all reactions of this class should have the same photochemical efficiency since, in general, secondary reactions are to be expected which may be different for different reactions. Investigation of other photochemical reactions with continuous absorption spectra will be interesting from this point of view. It seems possible that the photolysis of hydrogen bromide and hydrogen iodide should be very useful for the counting of quanta in a given beam in ultraviolet light.

in the continuous region. Accordingly, the class to which a photochemical reaction in which the halogen is the absorber belongs depends upon whether the wave length of light is in the region of band or continuous absorption.

The Halogen Hydrides.—The photographs of the absorption spectra of hydrogen chloride, bromide and iodide have been found to be continuous in structure.^{14,8} Tingey and Gerke⁸ have discussed the possibility as to whether the structure is apparently or actually continuous. It was concluded that the structure must be actually continuous if the spacing of the vibrational energy levels for the hypothetical electronic excited molecules would be approximately equal to those of the normal molecule. If it is granted that these absorption spectra are actually continuous, then it seems necessary that the primary action of the light produces a splitting of the molecule into two parts, which are presumably atoms. This assumption has in its support that no emission band spectra⁴⁰ corresponding to uni-univalent polar molecules have ever been observed.

With respect to the photochemical formation of the hydrogen chloride by the absorption of light by chlorine it is necessary to mention that the absorption of light in the continuous region and beginning with 3000 Å.³³ has been found to be effective when the gases are dry. In the presence of traces of water vapor wave lengths in the region of band absorption in the visible are also effective. Consequently the photochemical formation of hydrogen chloride in the absence of impurities is listed in the primary decomposition class. Moreover, this reaction in the presence of water vapor is not listed at all because the facts are not clear as to the role of the water vapor. For example, it has been found that in the case of the formation of hydrogen chloride one quantum of visible light would produce about a million molecules of hydrogen chloride,⁴¹ whereas it^{12,33} has been found that the reaction hardly proceeded at all in the visible region where the reaction mixture was carefully freed from water.

Oxygen.—The absorption spectrum of oxygen has been found to be similar to those of the halogens by the recent measurements of Leifson.¹⁴ In the far quartz and the near fluorite ultraviolet regions are the absorption bands of oxygen which at shorter wave lengths merge into a region of continuous absorption. Birge and Spomer⁷ attribute this continuous absorption to a dissociation of the molecule. It will be interesting to compare the photochemical activity of oxygen in the region of band and continuous absorption. Born and Gerlach³⁶ observed that the production of ozone was very great in the region of continuous absorption and that it seemed to fall off abruptly at greater wave lengths where band absorption began. The careful quantitative experiments of Warburg¹¹ in the region of band absorption show that oxygen forms ozone, but that 1.04 to 3.04

⁴⁰ Mulliken, *Phys. Rev.*, **26**, 1 (1925).

⁴¹ Bodenstein, *Z. physik. Chem.*, **85**, 351 (1913).

quanta are necessary to decompose one molecule of oxygen. This efficiency depends upon the wave length and the pressure. The formation of ozone is an example of both the "excited reactant" and "primary decomposition" types of photochemical reaction, depending upon whether the absorption spectrum consists of bands or is continuous in structure.

Ammonia.—The nature of the photochemical decomposition of ammonia has been uncertain, due to the fact that no definite conclusion could be drawn as to whether the absorption spectra were bands or continuous in structure. Examination of Leibson's recent data,¹⁴ however, shows that the structure consists of bands throughout the whole region of absorption. The decomposition of ammonia, therefore, belongs to the "excited reactant" type. It is interesting to note that the photochemical efficiency, which was quantitatively studied by Warburg¹⁵ and by Kuhn¹⁷ with monochromatic light depends upon the wave length of light.

Summary

The recent data on absorption spectra of gases entering into photochemical reaction, together with the older data, have made possible an extended study of the nature of the primary action of the absorbed light. In several cases band or line spectra have been observed for the absorbers which definitely classify these photochemical reactions into two widely known types of photochemical action which have been called in this paper the "excited reactant" and "excited sensitizer" types. In other cases not band spectra but continuous spectra were observed. Some authors have concluded as a necessary consequence of the most recent developments of the quantum theory of molecular spectra that the primary action of light in these cases is a dissociation of the molecule. Several examples of this class, which have been called the "primary decomposition" type in this paper, have been collected and compared with examples of the "excited reactant" and "excited sensitizer" types of photochemical reaction.

The quantum efficiencies of photochemical reactions as measured by the number of molecules which react per quantum of light absorbed are in accord with the suggestion; the chance for stimulation of photochemical action by excited molecules or atoms is not as great as by atoms produced from molecules by the primary action of the absorbed radiation.⁴²

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⁴² Since the manuscript was first written the writer has noted the interesting articles by Bonhoeffer and Steiner, *Z. physik. Chem.*, **122**, 287 (1926), on the continuous absorption in hydrogen iodide vapor and by Lewis, *Nature*, **119**, 493 (1927), on the constancy of the quantum yields on the photolysis of hydrogen iodide at very low pressures, which support the primary decomposition mechanism for those photochemical reactions with continuous absorption spectra.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY OF WEAK ACIDS IN AQUEOUS SULFATE SOLUTIONS

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It was shown in another place¹ that sulfates cause a marked rise in the activity coefficient of aqueous solutions of non-electrolytes. It was also shown in the previous article that the effect of salts was in general the same upon the activity coefficient of the undissociated part of weak acids and moderately strong acids as that upon non-electrolytes.

When we consider the total effect of sulfates upon the escaping tendency of acids of intermediate strength, the salting-out effect is greatly overshadowed by the removal of hydrogen ion to form hydrosulfate ion. Thus, in two solutions of a weak acid at a fixed activity, we have $(m_+ 'm_- ')/(m_+ m_-) = \gamma_{\pm}^2 / \gamma_{\pm}^{\prime 2}$, where m and m' are the molalities of the two solutions. If one of the solutions contains sulfate, there is formation of hydrosulfate ion with the removal of hydrogen ion from the solution. Consequently a larger molality of acid anion must be present to maintain equilibrium and the total molality will be increased.

Partially neutralizing this effect will be an increase in the activity coefficient of the undissociated molecules $m_u' / m_u = \gamma_u / \gamma_u'$. This effect will decrease the concentration of undissociated molecules, and the observed change in the molality of the acid, whose activity is held constant on adding sulfate, will be the algebraic sum of the change in the molality of acid anion and of undissociated molecules. The increase in total acid molality will be greater the larger the dissociation constant of the weak acid being studied.

Activity of Monochloro- and Dichloro-acetic Acids in Sulfate Solutions from Distribution Measurements

The same materials and methods were used as in the previous measurements.¹ The results are shown in Tables I, II and III. The first column gives the density of the aqueous phase, the second the ionic strength

TABLE I

DISTRIBUTION OF MONOCHLORO-ACETIC ACID BETWEEN MAGNESIUM SULFATE SOLUTIONS AND *n*-DIBUTYL ETHER AT 25°

$d_{4^{25^{\circ}}}$	$\mu(\text{MgSO}_4)$	m	n	m°	m°/m
1.003	0.242	0.1012	0.004554	0.0960	0.949
1.010	.492	.1044	.004661	.0981	.940
1.023	.970	.1055	.004783	.1008	.956
1.049	1.880	.1035	.004992	.1050	1.014

¹ Randall and Failey, *Chem. Rev.*, **4**, No. 3, (1927). The notation of that article will be used.

TABLE II

DISTRIBUTION OF MONOCHLORO-ACETIC ACID BETWEEN POTASSIUM SULFATE SOLUTIONS AND *n*-DIBUTYL ETHER AT 25°

$d \frac{25^\circ}{4^\circ}$	$\mu(\text{K}_2\text{SO}_4)$	m	n	m°	m°/m
1.008	0.300	0.1036	0.004356	0.0920	0.888
1.039	1.000	.1135	.004358	.0920	.811
1.058	1.500	.1128	.004298	.0910	.807
1.078	2.000	.1173	.004372	.0921	.785

TABLE III

DISTRIBUTION OF DICHLORO ACETIC ACID BETWEEN MAGNESIUM SULFATE SOLUTIONS AND *n*-DIBUTYL ETHER AT 25°

$d \frac{25^\circ}{4^\circ}$	$\mu(\text{MgSO}_4)$	m	n	m°	m°/m
1.009	0.242	0.1925	0.04606	0.1535	0.797
1.017	.492	.1952	.04795	.1580	.809
1.029	.970	.1663	.03423	.1215	.731
1.054	1.880	.1871	.03883	.1340	.716

of the added sulfate, the third the molality of the chloro-acetic acid in the aqueous phase and the fourth the mole fraction of the acid in the normal dibutyl ether phase. The fifth column gives the molality of pure acid in equilibrium with the ether at the same mole fraction of acid in the ether and the sixth the quotient of this quantity by the molality of acid in the sulfate solution.

Solubility of Weak Acids in Sulfate Solutions.—We also present in Table IV the results of some measurements by Rørdam² of the solubility of benzoic, *o*-toluyllic and *o*-nitrobenzoic acids in magnesium sulfate solutions at 25°. Cols. 1, 4 and 7 give the ionic strength of the added sulfate, Cols. 2, 5 and 8, the solubility of the acid and Cols. 3, 6 and 9, the ratio of the solubility in pure water to the solubility in the salt solution.

TABLE IV

SOLUBILITY OF BENZOIC, *o*-TOLUYLIC AND *o*-NITROBENZOIC ACIDS IN AQUEOUS MAGNESIUM SULFATE AT 25°

Benzoic			<i>o</i> -Toluylic			<i>o</i> -Nitrobenzoic		
$\mu(\text{MgSO}_4)$	$m(\text{acid})$	m°/m	$\mu(\text{MgSO}_4)$	$m(\text{acid})$	m°/m	$\mu(\text{MgSO}_4)$	$m(\text{acid})$	m°/m
0.00	0.02793	1.000	0.00	0.008783	1.000	0.00	0.04415	1.000
.02498	.02828	0.98804792	.04783	0.923
.04910	.02837	.984	.04792	.009044	0.971	.1000	.05011	.881
.1018	.02818	.991	.1000	.009124	.963	.2000	.05241	.842
.2029	.02796	.999	.2000	.009126	.962	.4000	.05490	.804
.4008	.02723	1.026	.6400	.009015	.974	.6400	.05633	.784
.7580	.02578	1.083	.9836	.008653	1.015	.9836	.05679	.777

Discussion.—The values of m°/m are plotted in Fig. 1 against the square root of the ionic strength of the added sulfate. Because of the number of variables and the complexity of the equilibria it is not practical to attempt to determine the activity coefficient of the various molecular

² Rørdam, *Thesis*, Copenhagen, 1925.

species in the solutions. If we define the activity as equal to the stoichiometric molality, m° , of a given solution of a weak acid in pure water, then m°/m will be analogous to the activity coefficient for a solution of the same activity in another solvent when the molality of the acid in equilibrium is m .

We note that the "activity coefficient" of the acid is lowered by a larger amount the larger the dissociation constant of the acid. This is in agreement with the assumption of a larger amount of hydrosulfate ion formed with the stronger acid. The salting-out effect is more noticeable with the

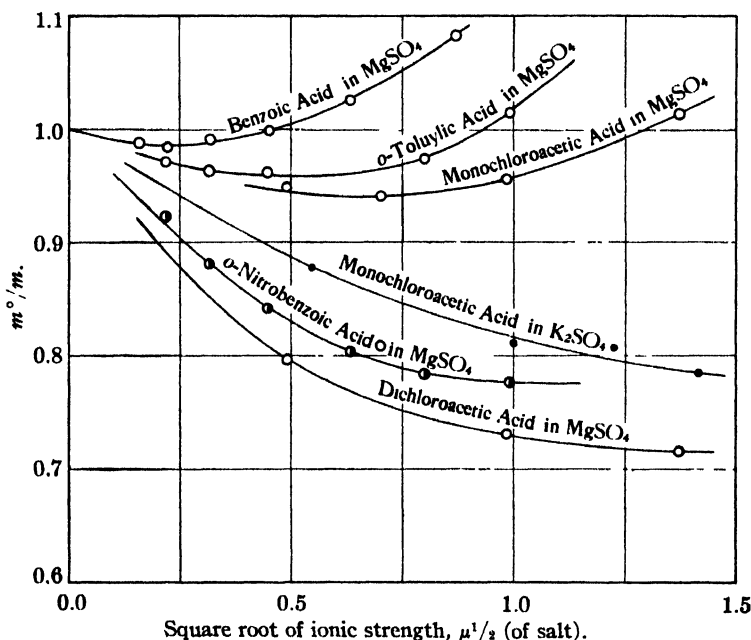


Fig. 1.—"Activity coefficients" at constant activity of weak acids in aqueous sulfate solutions at 25°.

weaker acids. The order of the effect of the potassium sulfate and magnesium sulfate upon dichloro-acetic acid is the same as the order of the effect of these salts on the activity coefficient of sulfuric acid,³ which must be considered a moderately weak acid. The activity coefficient of hydrobromic acid, a typical strong electrolyte, is greatly lowered by sulfates.⁴ This effect is almost wholly due to the formation of hydrosulfate ion. If we were to draw a curve for hydrobromic acid similar to that of Fig. 1, we should find that it lies lower than that of dichloroacetic acid for the same added sulfate.

³ See (a) Harned and Sturgis, *THIS JOURNAL*, **47**, 945 (1925). (b) Randall and Langford, *ibid.*, **49**, 1445 (1927).

⁴ See Livingston, *ibid.*, **48**, 45 (1926).

Summary

The distribution of monochloro- and dichloro-acetic acids between aqueous sulfate solutions and normal dibutyl ether has been measured.

The "activity coefficient" as measured by the ratio of the molality in pure water to that in a salt solution at a constant activity is determined by the salting-out effect of the sulfate on the undissociated part of a weak acid, and the amount of formation of hydrosulfate ion.

At constant ionic strength the "activity coefficient" is lower the greater the dissociation constant of the weak acid.

The "activity coefficient" is lowered to a greater extent by potassium sulfate than by magnesium sulfate.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE]

THE EFFECT OF SHAKING ON THE EVOLUTION OF GASES FROM SUPERSATURATED SOLUTIONS AND ITS IMPORTANCE FOR THE MEASUREMENT OF THE VELOCITY OF CERTAIN CHEMICAL REACTIONS

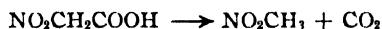
BY KAI JULIUS PEDERSEN

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Introduction

During the examination of the rate of decomposition of nitro-acetic acid in aqueous solution



by means of an apparatus described by J. N. Brønsted^{1,2} in which the pressure of the gas is measured during the reaction, it was found necessary to examine whether the gas was evolved sufficiently quickly to prevent a supersaturation effect. In order to get a quick evolution of the carbon dioxide the reaction flask was shaken horizontally. It was found that the supersaturation is very much less at a certain rate of shaking than with slower or quicker shaking. When the rate of shaking is not kept very constant, the supersaturation may, even when it is only small, as a consequence of this variability, cause a considerable error. The author thinks that this examination of the influence of the supersaturation may have some interest for other investigators who study the velocity of chemical reactions by measurement of the rate of gas evolution. Part 1 of this paper is an examination of the velocity of the evolution of carbon dioxide from supersaturated solution and its dependence upon the length and number per minute of the horizontal shakings of the reaction vessel. Part

¹ Brønsted and King, *THIS JOURNAL*, 47, 2523 (1925).

² Brønsted and Duus, *Z. physik. Chem.*, 117, 299 (1925).

2 is a mathematical treatment of the influence of supersaturation on the measurement of the velocity of a unimolecular reaction.

Part 1

The experiments were made at 18° in the Brönsted apparatus. The volume of the spherical part of the flask was 210 cc. Usually 100 cc. of solution was used; in one series of experiments only 60 cc. In each experiment 0.08–0.10 g. of sodium bicarbonate (about 0.001 mole) was weighed roughly in a little platinum bucket which was suspended at the top inside the apparatus so that it could be dropped into the solution after evacuation of the apparatus. The solution was usually 0.1 *M* hydrochloric acid; in some experiments a buffer solution: 0.06 *M* acetic acid + 0.04 *M* sodium acetate (*P_H* about 4.5).

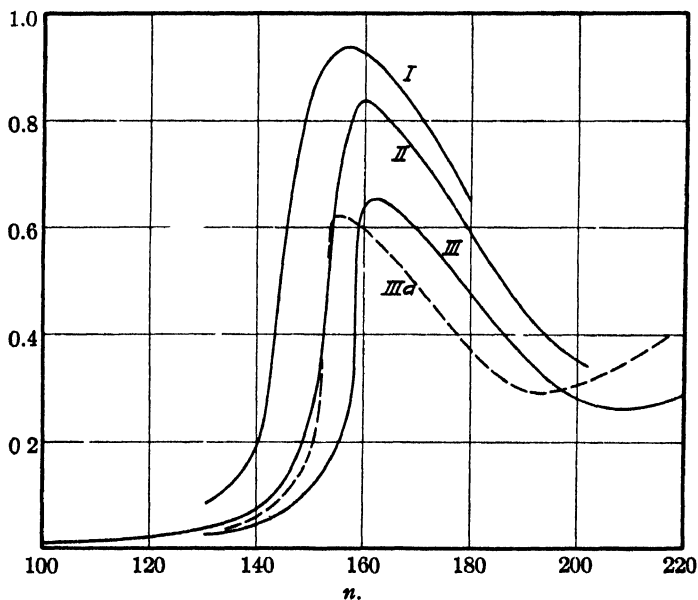


Fig. 1.—The velocity of the evolution of carbon dioxide from supersaturated solution.

In all the experiments (about 100) the rate of evolution of carbon dioxide followed the unimolecular law. Although the reaction in most cases was very quick, the agreement with the formula for the unimolecular reaction

$$kt = \text{constant} - \log P \quad (1)$$

(*k* being the velocity constant; *t*, the time in minutes; *P* = *p_∞* − *p*, the difference between the pressure *p_∞* above the solution after the reaction has finished and the pressure *p* at the time *t*) was very good; *k* was computed graphically by plotting log *P* against *t*. As seen from (1) it is not necessary to know the exact weight of the sodium bicarbonate nor the

time when it is dissolved. The shaking was stopped before the bucket was dropped and the reaction flask was kept quiet for some minutes until the first vigorous evolution of carbon dioxide had ceased, after which the pressure remained almost constant. Then the shaker was started and the rate of evolution from the supersaturated solution determined.

The finite velocity of the reaction in the aqueous phase, $\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$ (dissolved), was found to be without importance even in the quickest experiments with acetate buffer solutions. This is in agreement with the measurements of C. Faurholt,³ who has determined the velocity of the above reaction. At $P_{\text{H}} = 5$ he finds at 18° the velocity constant $k = 9$ (min.^{-1} , decad. logs) for the unimolecular reaction. In $0.1 M$ hydrochloric acid the reaction is practically instantaneous. Thus the velocity of the formation of dissolved carbon dioxide from the bicarbonate is, even at $P_{\text{H}} = 5$, ten times greater than the greatest velocity found for the evolution of gaseous carbon dioxide from the solution.

The evolution of carbon dioxide from its supersaturated solution is a limited reaction consisting of two opposing reactions: CO_2 (dissolved) $\rightleftharpoons \text{CO}_2$ (gas). As is well known, the constant h which has been measured is really the sum of the constants for the velocities of the two opposing reactions.

The experimental results are given in Fig. 1 and in Tables I-VI; h is the velocity constant (min.^{-1} , decad. logs), t is the time in minutes, n is the number of horizontal movements forwards and backwards of the reaction flask and l is the length in mm. of the single movement.

In Table I an experiment is given in full to give an idea of the accuracy of the measurements; $t = 0$ is the time when the shaker is started some time after the bicarbonate has been dissolved.

TABLE I
EVOLUTION OF CARBON DIOXIDE FROM SUPERSATURATED SOLUTION
Solution: 60 cc. of $0.1 M$ HCl. $n = 160$. $l = 7$ mm.

t , min.	p (m. Hg)	P	$\log P$	$\log P_0 - \log P$	h
0			0.074 ^a	0.000	..
1/4	7.02	0.86	.934-1	.140	(0.56)
1/2	7.28	.60	.778-1	.296	.59
3/4	7.46	.42	.623-1	.451	.60
1	7.58	.30	.477-1	.597	.60
1 1/4	7.66	.22	.342-1	.732	.59
1 1/2	7.72	.16	.204-1	.870	.58
1 3/4	7.78	.10	.000-1	1.074	.61
∞	7.88	.00		Mean value: $h = 0.60$	

^a Extrapolated.

In Fig. 1 the curves represent the following series of experiments, Curve I: 100 cc. of solution, $l = 18$ mm. (Table II); Curve II: 100 cc. of solution,

³ Faurholt, *J. chim. phys.*, **21**, 430 (1924).

$l = 12$ mm. (Tables III-IV); Curve III: 100 cc. of solution, $l = 7$ mm. (Table V); Curve IIIa: 60 cc. of solution, $l = 7$ mm. (Table VI).

TABLE II
Solution: 100 cc. 0.1 *M* HCl. $l = 18$ mm.

n	h	n	h
133	0.096	157	0.94
144	.43	161	.91
150	.84	166	.88
156	.93	178	.68

TABLE III
Solution: 100 cc. 0.1 *M* HCl. $l = 12$ mm.

n	h	n	h
100	0.0095	156	0.70
119	.021	158	.81
134	.052	162	.84
139	.060	163	.81
149	.22	166	.77
152	.37		

TABLE IV
Solution: 100 cc. 0.06 *M* acetic acid + 0.04 *M* sodium acetate. $l = 12$ mm.

n	h	n	h	n	h
113	0.016	155	0.62	172	0.72
130	.046	160	.86	177	.62
140	.077	160	.85	185	.52
148	.35	160	.81	191	.425
154	.62	164	.82	201	.35

TABLE V
Solution: 100 cc. 0.1 *M* HCl. $l = 7$ mm.

n	h	n	h	n	h
133	0.028	161	0.64	187	0.36
142	.040	161	.67	196	.27
147	.096	162	.64	198	.29
152	.13	166	.64	207	.26
154	.13	170	.59	209	.27
157	.25	177	.54	217	.275
159	.40	180	.49	224	.31
159	.50				

TABLE VI
Solution: 60 cc. 0.1 *M* HCl. $l = 7$ mm.

n	h	n	h	n	h
135	0.037	163	0.56	181	0.36
146	.103	165	.51	192	.285
151.5	.21	165	.53	201	.32
154	.61	166	.55	213	.37
160	.60	172	.48		

When n is about 160, h has a maximum. It falls quickly when n is increased or diminished, especially rapidly when n is diminished. In Curve

III it falls to half its value when n is diminished from 159 to 158 per minute. At greater values of n , h will pass through a minimum, as seen in the figure. The shape of the curves is similar to that of an ordinary curve of resonance. The maxima can be explained as due to resonance. When n has about that value corresponding with the maximum of h , the solution reaches the neck of the flask and falls down again. When it is shaken more quickly, it does not reach so far before it is stopped in its movement. It behaves like a pendulum, which prefers a certain number of oscillations per minute. If it is pushed at other intervals than its own time of oscillation it does not move so well.

Part 2

Let us consider the reactions (I) $A \rightarrow B + C$ (dissolved), velocity constant k (decad. logs) or k_n (natural logs), $k = k_n \log e$; (II) C (dissolved) $\rightleftharpoons C$ (gas), velocity constant h (decad. logs) or h_n (natural logs), h is the sum of the velocity constants for the two opposing reactions.

Let p denote the observed pressure of C (gas) at the time t . π is the pressure we would have obtained if there were no supersaturation. $\pi - p = \delta$ is a measure for the supersaturation. The subscripts 0 or ∞ denote that the pressures correspond with $t = 0$ or $t = \infty$. We put $P = p_\infty - p$ and $P_0 = p_\infty - p_0$.

We have the following two differential equations

$$\frac{d(P - \delta)}{dt} = k_n (P - \delta) \quad (2)$$

and

$$\frac{dp}{dt} = h_n \delta \quad (3)$$

They express, respectively, that Reaction (I) would give the unimolecular constant k_n in the experiment if there were no supersaturation, and that reaction (II) approaches the equilibrium as if it were a unimolecular complete reaction with the constant h_n . (2) and (3) are the exact mathematical expressions for the velocities of Reactions (I) and (II); (3) can also be written

$$-\frac{dP}{dt} = h_n \delta \quad (4)$$

By integration of (2) we have

$$P - \delta = (P_0 - \delta_0) e^{-k_n t} \quad (5)$$

which, together with (4), gives

$$\frac{dP}{dt} + h_n P = h_n (P_0 - \delta_0) e^{-k_n t} \quad (6)$$

By integration we obtain

$$P = (P_0 - \delta_0) \cdot \left[\frac{h_n}{h_n - k_n} e^{-k_n t} - \left(\frac{k_n}{h_n - k_n} - \frac{\delta_0}{P_0 - \delta_0} \right) e^{-h_n t} \right] \quad (7)$$

From (5) and (7) by subtraction

$$\delta = (P_0 - \delta_0) \cdot \left[\frac{k_n}{h_n - k_n} \cdot e^{-k_n t} - \left(\frac{k_n}{h_n - k_n} - \frac{\delta_0}{P_0 - \delta_0} \right) e^{-h t} \right] \quad (8)$$

Using decadic logarithms, (7) and (8) can be written as follows

$$P = (P_0 - \delta_0) \cdot \left[\frac{h}{h - k} 10^{-kt} - \left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0} \right) 10^{-ht} \right] \quad (9)$$

$$\delta = (P_0 - \delta_0) \left[\frac{k}{h - k} 10^{-kt} - \left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0} \right) 10^{-ht} \right] \quad (10)$$

(9) can be written as

$$kt = \log (P_0 - \delta_0) + \log \frac{h}{h - k} - \log \left[P + (P_0 - \delta_0) \left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0} \right) 10^{-ht} \right] \quad (11)$$

If $t = 0$ is the time when the reaction is started, and if we assume that there is no C present at $t = 0$, we have $\delta = 0$, in which case (11) simplifies to

$$kt = \log P_0 + \log \frac{h}{h - k} - \log \left[P + P_0 \frac{k}{h - k} \cdot 10^{-ht} \right] \quad (12)$$

If we ignore the supersaturation, the following simple formula would hold

$$kt = \log P_0 - \log P \quad (13)$$

When the shaking is kept uniform, and accordingly h is a constant, $\log \frac{h}{h - k}$ in (12) is constant and without importance for the determination of k . The other correction $\Delta = P_0 \frac{k}{h - k} 10^{-ht}$ decreases rapidly as t increases. If we require $\Delta < 0.01$ cm., before we take readings of p , we are sure to attain this by waiting until the time t determined by

$$\Delta < 10 \cdot 10^{-ht} < 10^{-2}. \quad ht > 3. \quad t > 3/h$$

(we assume $P_0 < 10$ cm. and $h > 2k$).

In Fig. 2, AB is the straight line we should get by plotting $\log P$ against t if there were no supersaturation ($P_0 = 8$ cm., $k = 0.03$, $h = \infty$). With supersaturation, say $h = 0.3$, we get the curve AB_1 by plotting $\log P$ against t . AB_1 very quickly fuses into the straight line A_1B_1 . Thus the supersaturation only causes a parallel displacement of the straight line. The magnitude of this displacement is determined by the term $\log h/(h - k)$. Δ determines how quickly the curve AB_1 fuses into the straight line A_1B_1 .

If Reaction II had taken place in a homogeneous phase, h would be constant at constant temperature. In the present case Reaction II is a heterogeneous reaction and h varies with the rate of shaking. We shall find what influence it will have if h changes to h' at the time t_1 during the reaction. From (11) we get

$$k(t - t_1) = \log(P_1 - \delta_1) + \log \frac{h'}{h' - k} - \log \left[P + (P_1 - \delta_1) \left(\frac{k}{h' - k} - \frac{\delta_1}{P_1 - \delta_1} \right) 10^{-h(t-t_1)} \right] \quad (14)$$

From (5) we get, putting $\delta_0 = 0$,

$$\log(P_1 - \delta_1) = \log P_0 - kt_1 \quad (15)$$

and from (5) and (10)

$$\frac{\delta_1}{P_1 - \delta_1} = \frac{k}{h - k} - \frac{k}{h' - k} 10^{-(h-k)t_1} \quad (16)$$

If we substitute (15) and (16) in (14) we get

$$kt = \log P_0 + \log \frac{h'}{h' - k} - \log \left[P + P_0 \frac{k}{h - k} \left(10^{-(h'(t-t_1) + ht_1)} - \frac{h' - h}{h' - k} 10^{-(h'(t-t_1) + ht_1)} \right) \right] \quad (17)$$

which gives an expression for k when $t \geq t_1$. It shows that the change in supersaturation due to the change in h at $t = t_1$ causes a new parallel displacement of the straight line whose slope determines k . If $P_0 = 8$ cm., $k = 0.03$, $h = 0.3$, when $t < 5$ min., but $h = 0.6$ when $t > 5$ min., we get the curve ACB₂ in Fig. 2. CB₂ fuses into the straight line A₂B₂ parallel to AB. The magnitude of the extra displacement is determined by the change in the constant term of equation (17) compared with that of (12) which holds for $t \leq t_1$. The

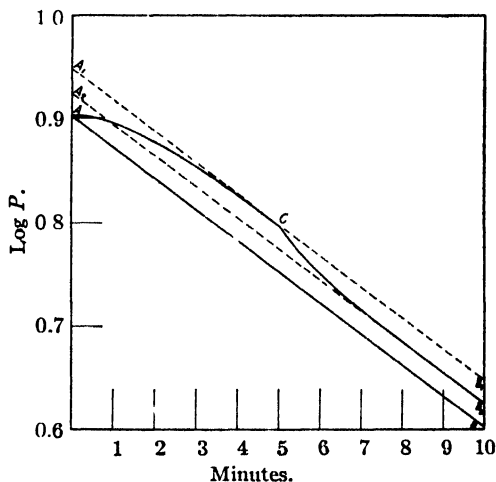


Fig. 2.--The effect of supersaturation on a uni-molecular reaction.

$$\Delta_2 = -P_0 \frac{k}{h - k} \frac{h' - h}{h_1 - k} 10^{-(h'(t-t_1) + ht_1)}$$

shows how quickly this second displacement takes place, while

$$\Delta_1 = P_0 \frac{k}{h - k} 10^{-(h'(t-t_1) + ht_1)}$$

expresses the changed velocity for the first displacement for $t > t_1$. Of course Δ_1 will only play a part when the change in h to h' occurs very soon after the start, that is, before the first displacement has finished.

If we wish to calculate how great a change in h we can allow during the reaction, it is obviously sufficient to consider the corrections in the

constant term. We, therefore, put $\Delta_1 = \Delta_2 = \Delta = 0$. We get inste, of (12) and (17) the simpler formulas

$$0 < t < t_1: kt = \log P_0 + \log \frac{h}{h-k} - \log P \quad (18)$$

$$t_1 < t: kt = \log P_0 + \log \frac{h'}{h'-k} - \log P \quad (19)$$

(19) can be written as follows

$$t_1 < t: kt = \log P_0 + \log \frac{h}{h-k} - \log \left(P \frac{h}{h-k} \frac{h'-k}{h'} \right)$$

which by comparison with (18) gives

$$\frac{\Delta P}{P} = \frac{h}{h-k} \frac{h'-k}{h'} - 1 = \frac{k}{h-k} \frac{h'-h}{h'}$$

$$\frac{\Delta h}{h} = \left(\frac{h}{k} - 1 \right) \frac{\Delta P}{P}$$

If we require that $\Delta P/P < 0.2\%$, the permissible variation in h is determined by

$$\frac{\Delta h}{h} < \left(\frac{h}{k} - 1 \right) 0.2\%$$

Examples

While the free undissociated nitro-acetic acid is stable in aqueous solution, the decomposition of the nitro-acetate ion follows the unimolecular law.⁴ The constants are at 18° 0.0241 and at 20° 0.0316 (min.⁻¹, decad. logs).

1. In an experiment on the decomposition of the nitro-acetate ion we have $k < 0.03$. $P_0 < 10$ cm. We use 100 cc. of solution. We shake so that we get as little supersaturation as possible: $l = 18$ mm., $n = 158$ (the maximum of Curve I in Fig. 1). From the figure we find $h = 0.94$. We have $\Delta < 10 (0.03/0.9) 10^{-0.94t}$. $t = 1$, gives $\Delta < 0.04$, $t \geq 2$, gives $\Delta < 0.005$. If we allow an error of 0.01 cm. in P , we can start the readings two minutes after the dissolution of the nitro-acetic acid.

In h we can allow a variation of $((0.94/0.03) - 1) 0.2 = 6\%$. From Curve I we find that n must be kept within the limits $152 < n < 163$.

2. If we shake more rapidly, say $n = 190$, $l = 12$ mm., the conditions become much less favorable for a good result, as seen from the following calculations. From Curve II in Fig. 1 we find $h = 0.43$; $\Delta < 10 (0.03/0.40) 10^{-0.43t}$.

The induction period is much longer

t	1	2	3	4	5
Δ	0.28	0.10	0.04	0.014	0.006

We must wait five minutes for the first reading. The permissible variation in h is $((0.43/0.03) - 1) 0.2 = 2.6\%$. From the curve we find that n

⁴ Pedersen, *Trans. Faraday Soc.*, 23, 316 (1927).

must be kept within the limits $189 < n < 191$. A comparison of the two examples makes clear of how great importance it may be to know how to do the shaking in order to get the best effect.

In conclusion I wish to thank Professor Dr. Niels Bjerrum, whose advice and helpful criticism of my work have been of great value.

Summary

The supersaturation error in measurements of velocity of chemical reactions by rate of gas evolution has been examined.

The velocity of the evolution of carbon dioxide from supersaturated solution follows the unimolecular law. The dependence of its velocity constant h on the number of horizontal shakings n per minute has been determined. h has a maximum and falls rapidly when n is diminished or increased.

A mathematical expression for the velocity of the evolution of gas in the course of the reaction $A \rightarrow B + C$ (dissolved), followed by the reaction C (dissolved) $\rightleftharpoons C$ (gas), has been derived.

The importance of the results for the measurement of a fairly quick unimolecular reaction has been discussed.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 557]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. I SALT EFFECT ON THE VELOCITY OF OXIDATION OF AMMONIA. II. COMPARISON OF THE VELOCITY WITH VARIOUS REDUCING AGENTS

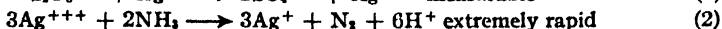
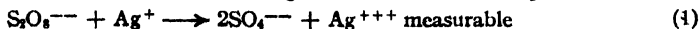
By CECIL V. KING

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I. Introduction

It has been shown that persulfates react with ammonia, in alkaline solutions, in the presence of silver salts, with a measurable velocity,¹ and Yost has represented the reaction as taking place in two steps, as follows (the silver ion, however, being in an ammonia complex):



There seems to be no question that trivalent silver is formed, as indicated by two things: the analysis of the insoluble compound formed when persulfates and silver salts are mixed, and the fact that the reaction rate, when ammonia or chromic salts are oxidized, is proportional to the *first* power of the silver-ion concentration.

¹ (a) Marshall, *Proc. Roy. Soc. Edinburgh*, 23, 163 (1900). (b) Yost, *This Journal*, 48, 374 (1926).

Yost found that when this reaction was carried out in alkaline solution increase in ammonia concentration increased the velocity of reaction, while increase in hydroxide concentration decreased it. Since in any one experiment ammonia and hydroxyl ions both disappear and the silver-ion concentration remains constant, rather good "pseudo-unimolecular" rate constants can be obtained. Since Yost attributes the measurable velocity entirely to reaction (1), he concludes that the effect of increased ammonia concentration is to increase the concentration of a silver ion with more ammonia groups attached than in $\text{Ag}(\text{NH}_3)_2^+$, and that this higher complex makes reaction (1) faster. The effect of hydroxide he treats rather as a specific effect than a general salt effect, though he suggests that perhaps "a decrease in the activity coefficient of peroxysulfate ion is superposed upon the effect of producing a less reactive substance" $[\text{Ag}(\text{NH}_3)_2\text{OH}]$. It is the purpose of this paper to show that the effect of hydroxides is not a specific but is a perfectly general salt effect; to show that the reaction is "pseudo-unimolecular" only in a certain range of salt concentration (that is, where change in ionic concentration during the course of the reaction counteracts the loss of ammonia); and to discuss the question of possible dependency of the velocity of the reaction on the nature of the reducing agent.

Theoretical

If the velocity-determining reaction is $\text{S}_2\text{O}_8^{--} + \text{Ag}^+ \longrightarrow \text{Ag}^{+++} + 2\text{SO}_4^{--}$, then, according to Brönsted's theory of kinetic salt effect,² the expression for the velocity should be

$$V = k' C_{\text{S}_2\text{O}_8^{--}} \cdot C_{\text{Ag}^+} \cdot \frac{f_{\text{S}_2\text{O}_8^{--}} \cdot f_{\text{Ag}^+}}{f_{(\text{S}_2\text{O}_8, \text{Ag})^{--}}}$$

where f represents activity coefficient; and we may consider that $f_{(\text{S}_2\text{O}_8, \text{Ag})^{--}}$ (the activity coefficient of the first complex formed between Ag^+ and $\text{S}_2\text{O}_8^{--}$) is approximately equal to f_{Ag^+} , since both are univalent ions, thus reducing the velocity expression to

$$V = k' C_{\text{S}_2\text{O}_8^{--}} \cdot C_{\text{Ag}^+} \cdot f_2$$

where $f_{\text{S}_2\text{O}_8^{--}} = f_2$ if $f_{\text{S}_2\text{O}_8^{--}}$ approximates the activity coefficient of any bivalent ion. Then

$$k = k' f_2$$

where k = the observed rate constant and k' = the theoretical rate constant in a solution containing no ions; and k as measured and plotted later in this paper is directly proportional to the activity coefficient of a bivalent ion, provided that Brönsted's theory is correct and that the velocity is actually determined by the reaction assumed.

Even if the second reaction



² Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); *ibid.*, **115**, 337 (1925); Lecture, Columbia University, Columbia University Press, New York City, 1926.

were slow, according to Brönsted's theory the salt effect would be small and linear and the total salt effect would be nearly the same; but if this were true it should be evidenced by accumulation of the trivalent silver and precipitation of the insoluble black compound, and this is not the case.

Experimental

Method of Measuring Velocity.—Since in a closed system the pressure of nitrogen above the solution is directly proportional to the amount of persulfate decomposed (provided thorough shaking of the reaction vessel insures equilibrium at all times), the velocity can be measured by following this pressure. The same type of apparatus described before for measurements of this sort was used.³ The space above the solution in the velocity apparatus was evacuated to practically the vapor pressure of the solution; evacuation was continued for as short a time as possible in order to avoid undue volatilization of ammonia. The volume of solution used was 100 cc. and the space above the solution was about 100 cc. It can be shown from the vapor pressure of ammonia from the solutions used that the amount of ammonia in the gas phase was always considerably less than 1% of the total amount present, so this factor is unimportant.

In making the measurements, suitable amounts of standard persulfate, ammonia, hydroxide and salt solutions were mixed and made up to 98 cc., put in the reaction flask and allowed to come to temperature. A 2 cc. portion of standard silver nitrate solution was carefully measured into a glass capsule with a small glass hook near its open end, and this capsule suspended from a platinum loop fused into the side of the neck of the reaction flask. The flask was closed and the apparatus evacuated with shaking to aid evolution of dissolved air in the solution, the apparatus closed, the pressure read and the capsule with the silver nitrate dropped into the solution and thoroughly mixed by the shaking. The time was noted from the time the silver nitrate solution became thoroughly mixed with the other solution.

The rate constants were calculated in the same way as Yost's, that is, from the integrated form of the equation

$$\frac{dC_{\text{SO}_4^{--}}}{dt} = k \cdot C_{\text{SO}_4^{--}} \cdot C_{\text{Ag}^+}$$

Solutions Used.—Potassium persulfate was prepared by recrystallizing the c. p. salt two or more times from water between 50 and 0°; the crystals were drained on a cotton plug in a funnel, washed with cold water, dried by sucking dried, dust-free air through them for two or three hours and further allowed to stand several days in a desiccator over sulfuric acid before use. Standard solutions were made by direct weighing of the salt, and were made fresh every four or five days.

C. p. ammonia water was diluted to the desired strength and standardized by running a sample from a pipet into excess of standard hydrochloric acid, titrating back with standard potassium hydroxide with methyl red as indicator.

Potassium and sodium hydroxides were made from saturated solutions that had stood for some time to allow the insoluble carbonates to settle out, and standardized

³ (a) Brönsted and Daus, *Z. physik. Chem.*, 117, 299 (1925); (b) Brönsted and King, *THIS JOURNAL*, 47, 2523 (1925).

against resublimed benzoic acid. The solutions were made in carbon dioxide-free, distilled water and protected from the air.

Potassium and sodium nitrates were recrystallized from the c. p. salts, dried at 100°, pulverized and dried again at 100° and allowed to stand in a desiccator over sulfuric acid for several days before use; the standard solutions were made by weighing the salts.

Silver nitrate was made by recrystallizing the c. p. salt. A 0.15 *M* solution was made by weighing the salt, and a 2 cc. portion was pipetted out of this same solution for every experiment. The solution was kept in a dark closet. The 2cc. pipet used could easily deliver the same amount with a maximum error of less than 0.5%, well within the error of measurement of the reaction-velocity constants.

In all experiments the concentration of the catalyst was the same; the concentration of ammonia was the same (within 0.5%) and was much higher than that of the persulfate; and the concentration of persulfate was the same (except in two experiments which are noted later). The concentration of persulfate used was chosen to give a suitable increase in pressure in the apparatus, and the concentration of ammonia was chosen so that the proportion oxidized was not too great, and the change in ionic concentration during the reaction would practically balance the loss in ammonia, except in a few experiments noted later. All measurements were made at $20^\circ \pm 0.01^\circ$.

Results of the Measurements.—Experiment 40 in Table I shows the results of a typical experiment with a solution containing sufficient potassium hydroxide so that no NH_4^+ ion was formed during the reaction, that is, so that the solution did not become much less alkaline. In some experiments such a small amount of potassium hydroxide was used that it would all be neutralized before the reaction was over; NH_4^+ is then formed and the ammonia disappears much more rapidly. In these cases the velocity constants fell off towards the end of the reaction and only those over the first half of the reaction were used for the averages. Experiments 28 and 26, Table I, show how the "constants" fall off when no potassium hydroxide is used and so ammonia disappears both from the oxidation and neutralization of H^+ ion formed—even though sufficient inert salt (potassium nitrate) is present so that the change in ionic concentration is small.

TABLE I
RESULTS OF TYPICAL EXPERIMENTS (TEMPERATURE, 20°)

Expt. 40 0.04 <i>N</i> $\text{K}_2\text{S}_2\text{O}_8$, 0.08 <i>N</i> NH_3 , 0.20 <i>N</i> KOH , 0.003 <i>N</i> AgNO_3		Expt. 28 0.04 <i>N</i> $\text{K}_2\text{S}_2\text{O}_8$, 0.08 <i>N</i> NH_3 , 0.16 <i>N</i> KNO_3 , 0.003 <i>N</i> AgNO_3		Expt. 26 0.04 <i>N</i> $\text{K}_2\text{S}_2\text{O}_8$, 0.08 <i>N</i> NH_3 , 0.20 <i>N</i> KNO_3 , 0.003 <i>N</i> AgNO_3	
Time, min.	<i>k</i>	Time, min.	<i>k</i>	Time, min.	<i>k</i>
30	2.74	15	2.44	20	2.25
40	2.66	35	2.42	40	2.27
50	2.68	55	2.42	60	2.23
60	2.72	85	2.30	80	2.19
70	2.69	125	2.33	100	2.17
80	2.71	155	2.25	120	2.17
100	2.73	215	2.21	170	2.07
120	2.72	245	2.21	290	2.03
140	2.68				
170	2.72				
Mean	2.71				

In Table II are given the mean constants for a number of experiments in which varying amounts of potassium hydroxide, sodium hydroxide, potassium nitrate and sodium nitrate were added. When potassium nitrate and sodium nitrate were used, it was, as stated, necessary to start with some alkali present, if the "pseudo-unimolecular" constants were to be obtained; and so 0.02 *N* potassium hydroxide was present in all these experiments, this being about the minimum amount possible. It is unfortunate for the comparison between the effect of sodium and potassium ions that sodium ion could not constitute the entire positive ion present in those experiments with sodium ion; but due to the difficulty of preparing pure sodium persulfate this was not attempted. It would also have been possible to prepare pure ammonium persulfate and then have

TABLE II
CONSTANTS (TEMPERATURE, 20°)

Summary of effect of KOH 0.04 <i>N</i> K ₂ S ₂ O ₈ , 0.08 <i>N</i> NH ₃ , 0.003 <i>N</i> AgNO ₃			Summary of effect of KNO ₃ 0.04 <i>N</i> K ₂ S ₂ O ₈ , 0.08 <i>N</i> NH ₃ , 0.02 <i>N</i> KOH, 0.003 <i>N</i> AgNO ₃		
<i>C</i> _{KOH} , <i>N</i>	Total salt, equiv. concn.	<i>k</i>	<i>C</i> _{KNO₃} , <i>N</i>	Total salt, equiv. concn.	<i>k</i>
0.02	0.063	4.22	..	0.063	4.22
.02	.063	4.23	..	.063	4.23
.04	.083	3.64	0.02	.083	3.58
.08	.123	3.25	.04	.103	3.17
.08	.123	3.28	.08	.143	2.71
.12	.163	3.05	.10	.163	2.50
.12	.163	3.05	.12	.183	2.42
.16	.203	2.85	.14	.203	2.23
.20	.243	2.68	.16	.223	2.13
.20	.243	2.71			
Summary of effect of NaOH 0.04 <i>N</i> K ₂ S ₂ O ₈ , 0.08 <i>N</i> NH ₃ , 0.003 <i>N</i> AgNO ₃			Summary of effect of NaNO ₃ 0.04 <i>N</i> K ₂ S ₂ O ₈ , 0.08 <i>N</i> NH ₃ , 0.003 <i>N</i> AgNO ₃ , 0.02 <i>N</i> KOH		
<i>C</i> _{NaOH} , <i>N</i>	Total salt, equiv. concn.	<i>k</i>	<i>C</i> _{NaNO₃} , <i>N</i>	Total salt, equiv. concn.	<i>k</i>
0.02	0.063	4.30	0.125	0.188	2.62
.04	.083	3.84	.175	.238	2.41
.08	.123	3.52			
.12	.163	3.32			
.16	.203	3.15			
.16	.203	3.21			
.20	.243	3.11			

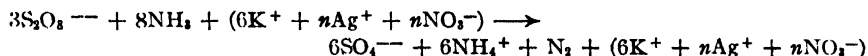
Summary of results with no inert salt present
0.08 *N* NH₃, 0.003 *N* AgNO₃

<i>C</i> _{K₂S₂O₈} , <i>N</i>	<i>C</i> _{NH₄⁺} at start, <i>N</i>	Total salt, equiv. concn.	<i>k</i> (start)
0.02	0.0013	0.024	7.34-7.00
.02	.0013	.024	6.89-6.71
.04	.0013	.044	6.44-5.94
.04	.0013	.044	5.78-5.40

included the ammonia formed in the alkaline solution from this in the total ammonia concentration. This was also not attempted, chiefly because a qualitative, not a quantitative, comparison between the potassium and sodium ions was desired. Of course, only a qualitative comparison between the hydroxide and nitrate ions can be made, as these must both be present in all solutions.

It was feared that when a solution became low in hydroxyl-ion concentration, some nitrate might be formed—that is, not all the oxidation resulted in nitrogen gas.⁴ But in no case was there evidence that less nitrogen was evolved than in the most alkaline solutions.

In Table III are given full data for experiments made with the lowest possible salt concentrations. No ionic substances were present except those actually necessary; and in Experiments 45 and 46 the persulfate concentration was reduced to the minimum necessary for accurate measurements by the method used. It was known that ammonia would disappear rapidly, and that the ionic concentration would increase, as indicated in the equation



(ions whose concentrations are unchanged being enclosed in the parentheses). Since both these effects would decrease the velocity, it is to be expected that the "constants" would fall off very rapidly, and that this happened is shown in the table. Only the very first "constants" can give a measure of the true velocity for the ionic concentrations specified for these solutions in Table II; and these values, due to the difficulty of accurate measurement, are less accurate than those in Table II. Never-

TABLE III
EXPERIMENTS WITH LOW SALT CONCENTRATIONS (TEMPERATURE, 20°)

Expts. 43 and 44			Expts. 45 and 46		
0.04 N K ₂ S ₂ O ₈ , 0.08 N NH ₃ , 0.003 N AgNO ₃			0.02 N K ₂ S ₂ O ₈ , 0.08 N NH ₃ , 0.003 N AgNO ₃		
Time, min.	k (43)	k (44)	Time, min.	k (45)	k (46)
4	6.44	5.78	4	7.36	6.89
6	5.94	5.40	6	7.00	6.71
8	5.43	5.24	8	6.72	6.61
10	5.43	5.11	10	6.60	6.30
15	5.13	4.90	15	6.41	6.24
20	4.99	4.85	20	6.39	6.27
30	4.74	4.72	30	6.24	6.13
60	4.54	4.49	40	6.33	6.12
80	4.41	4.37	50	6.11	5.94
95	4.37	4.38	60	6.17	5.91

⁴ (a) Marshall, *Proc. Roy. Soc. Edinburgh*, 23, 168 (1900); (b) Marshall and Inglis, *ibid.*, 24, 88 (1902).

theless, they show the order of magnitude of the velocity and indicate very clearly how different it is in these solutions of lowest ionic concentration.

It is evident that in solutions of very low ionic concentration the salt effect due to changing ionic concentration during the course of the reaction entirely masks the character of the reaction. It is necessary, of course, to determine the character of such a reaction in high concentrations of some neutral salt, where the change will have little influence.

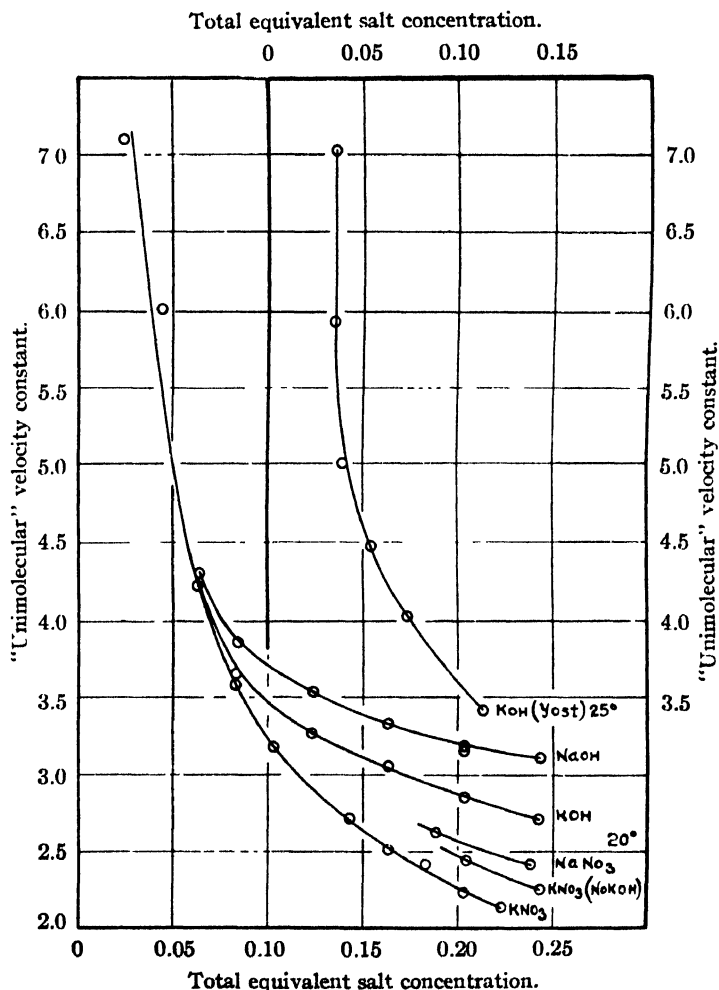


Fig. 1.—Effect of added salts on the persulfate-ammonia reaction.

Discussion of Results

The results given in Tables II and III are plotted in Fig. 1. A glance at this figure shows again how useless it is to record a velocity constant

for a reaction between ions unless not only their concentration but the total ionic concentration of the solution is given. This is especially true for very low salt concentrations where the velocity changes very rapidly with changing salt concentration.

The curves make it plain that the effect is not a specific one for hydroxides, since the effect of the salts used is of the same character and magnitude. Both positive and negative ions show an effect, since changing either one changes the salt effect. Sodium ion shows less effect than potassium ion, and this is in agreement with the measurements of the effect of sodium and potassium salts on activity coefficients of ions by other means, for example, from solubility measurements. Slightly soluble salts are as a rule less soluble in sodium salts than in potassium salts at corresponding concentrations,⁵ and this means that the activity coefficient of the saturating salt is greater in the sodium salt than in the potassium salt solution. Here, since k is proportional to f_2 , it is seen that f_2 is greater in the presence of the sodium salt than in the presence of the potassium salt.

There are in the literature no direct comparisons available between the effects of hydroxides and nitrates on the activity coefficients of other ions. However, as a rule hydroxides have a greater "salting out effect" than other ionic substances, both on non-electrolytes and electrolytes.⁶ This would indicate that the activity coefficients of other ions should be lower in the presence of nitrates than in the presence of hydroxides, and this is in accordance with the data here presented and shown in Fig. 1.

It is impossible to extrapolate the curves to zero concentration and so get any accurate measure of the absolute magnitude of the salt effect, but the sign, general character and magnitude agree with the Brönsted theory. It is sufficient to say that in this solution, containing some bivalent and some monovalent ion, at a concentration of 0.04 N , f_2 = about 0.40, the velocity of the reaction should be only about four-tenths its value in a solution of zero ionic concentration.

In the inserted figure some of Yost's measurements have been replotted on the same scale as the others. The data are given in Table IV. The first two measurements were with ammonium persulfate, with no addition of potassium hydroxide, and, as noted before, these "constants" fall off rapidly during the reaction. Consequently the first "constants" only are taken and these are recalculated to the same concentration of ammonia as the other measurements, using Yost's curve for the effect of ammonia on the reaction rate to make this correction. The values obtained are,

⁵ See, for example, (a) Brönsted, *THIS JOURNAL*, **44**, 877 (1922); (b) *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **4**, No. 4 (1921).

⁶ See, for example, Rørdam, "Studies on Activity," *Dissertation*, H. H. Thieles Bogtrykkeri, Copenhagen, 1925, pp. 44-45; Brönsted, *THIS JOURNAL*, **42**, 785 (1920).

of course, not very accurate but it is evident that the curve as a whole is of exactly the same type and the salt effect of the same magnitude as found in the present investigation. It is difficult to make a direct comparison due to the difference in ammonia concentration and difference in temperature (Yost's measurements were at 25°).

TABLE IV
YOST'S MEASUREMENTS AT 25°

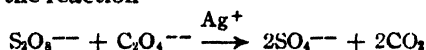
$C_{S_2O_8^{--}}$	C_{Ag^+}	C_{NH_3}	C_{KOH}	Total salt, equiv. concn.	k
0.0138 <i>M</i>	0.0059	0.1123	0.0355	7.00 ^a
.0138	.0059	.06870345	5.90 ^a
.0086	.005	.0383	0.017	.039	5.00
.0086	.005	.0383	.034	.056	4.45
.0086	.005	.0383	.0519	.0741	4.01
.0086	.005	.0383	.0904	.1126	3.41

Calculated for $C_{NH_3} = 0.0383$ *N*.

II. Comparison of the Velocity with Various Reducing Agents

According to the assumptions made, any substance oxidized by persulfate in the presence of silver ion (at negligible speed otherwise) should be oxidized at the same rate, the total salt concentration being the same, provided the second reaction is very rapid, and in case the persulfate and silver ions are in the same condition of solvation, etc. At least, no such oxidation should be faster than the oxidation of Ag^+ to Ag^{++} . Now Marshall and Inglis have measured the velocity of oxidation of NH_4^+ to NO_3^- by persulfate in the presence of silver ion at 25°, ^{4b} with only NH_4^+ , $S_2O_8^{--}$ and $AgNO_3$ present, and also in the presence of other salts. Yost has measured the velocity of oxidation of chromic ion by persulfate in the presence of silver ion.⁷ Some typical total salt concentrations and rate constants (those of Marshall and Inglis recalculated in the same manner as those in this paper) are given in Table VI. From these figures it seems quite possible that the velocities of the NH_4^+ and the Cr^{+++} oxidations are controlled in exactly the same way, the small differences being due to salt effect. But the ammonia oxidation is 10 times as fast; Yost concludes that this is due to the fact that not Ag^+ but $Ag(NH_3)_2^+$ is reacting. This appears to be a plausible explanation.

The author has also carried out some experiments involving silver ion as the catalyst for the reaction



In these solutions the Ag^+ was expected to be in the same state of solvation as in the Cr^{+++} and NH_4^+ solutions and, consequently, the velocity of reaction should be about the same. But the experiments indicated that it was about 4000 times as fast as in the Cr^{+++} and NH_4^+ oxidations,

⁷ Yost, *THIS JOURNAL*, 48, 152 (1926).

and 300 to 400 times as fast as in the ammonia oxidation. The results of one experiment are given in Table V and also in Table VI.

TABLE V
EXPERIMENTAL RESULTS

0.02 <i>N</i> Na ₂ C ₂ O ₄	}	Total salt concentration, 0.03 <i>N</i>
0.01 <i>N</i> K ₂ S ₂ O ₈		
0.00002 <i>N</i> Ag ₂ SO ₄		
Time, min.	Pressure of CO ₂ , cm. Hg	<i>k</i>
10	1.10	989.0
20	2.27	1162
30	3.11	1184
40	3.49	1208
60	4.33	1127
90	5.57	1047
∞	6.10	..

TABLE VI
TYPICAL VALUES

Total salt equiv. concn.	<i>k</i>	
1.0	0.218	Marshall and Inglis, NH ⁺ oxidation (25°)
0.5	.267	
0.2-0.36	0.30-0.36	Yost, Cr ⁺⁺⁺ oxidation (25°)
.2	2.25-3.25	King, NH ₃ oxidation (20°)
.03	7.0	King, NH ₃ oxidation (20°)
.03	1100-1200	King, C ₂ O ₄ ⁼ oxidation (20°)

These experiments were not continued, as it was difficult to reproduce results within less than 10 to 15%, and only with certain concentrations of reactants was the reaction as nearly "pseudo-unimolecular" as the above example. Nevertheless, it seems that the mechanism of the silver ion catalysis may not be altogether explained yet. It is possible that the nature of the reducing agent influences the velocity, in spite of the other evidence to the contrary.

Summary

I. The effect of various salts on the velocity of oxidation of ammonia by persulfate, catalyzed by silver ion, has been measured, and the following conclusions have been reached.

1. The effect of hydroxides, as measured by Yost, is not specific, but a general salt effect (except in so far as the equilibrium $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ is concerned).

2. The salt effect is of the sign, general character and magnitude predicted by the Brönsted theory of salt effect, assuming the velocity-determining reaction to be that deduced by Yost.

3. The specific effect of the ions K⁺, Na⁺, OH⁻ and NO₃⁻ is in accord with their effect on the activity coefficient of other ions as indicated by solubility and other measurements.

4. It is pointed out again that the magnitude of the salt effect on velocity of reaction between ions is very great in dilute solutions, and that at low concentrations changing salt concentration during the course of a reaction may mask the true character of the reaction.

II. Finally, it is shown that in the case of the reaction $\text{S}_2\text{O}_8^{--} + \text{C}_2\text{O}_4^{--} \xrightarrow{\text{Ag}^+} 2\text{SO}_4^{--} + 2\text{CO}_2$, the velocity is not as predicted from the other reactions.

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FLUORESCENCE IN MIXTURES OF AMMONIA AND MERCURY VAPOR

By ALLAN C. G. MITCHELL

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Introduction

While making experiments on the decomposition of ammonia by optically excited mercury vapor, Dickinson and Mitchell¹ observed a greenish fluorescence which appeared when a mixture of ammonia at a few millimeters' pressure and mercury vapor at room temperature was illuminated by the radiation from a cooled quartz mercury arc; they showed that the resonance radiation 2537 Å. was necessary to the production of this fluorescence. Observations with a direct vision spectroscope showed the fluorescence to be a diffuse band with a maximum around 5100 Å. Photographs with a quartz prism spectrograph showed an additional diffuse band in the ultraviolet with a maximum around 3370 Å. The green fluorescence was also observed visually when nitrogen was used instead of ammonia.

In the present experiments the ultraviolet fluorescence and the conditions under which it is excited were examined further.

Experimental Arrangement

A spherical resonance vessel (volume about 500 cc.) with a plane quartz window sealed to one end with sealing wax was connected to a vacuum system. About 2 cc. of mercury was placed in the resonance vessel to give a partial pressure of mercury corresponding to its vapor pressure at room temperature. Ammonia, nitrogen, hydrogen and argon could be admitted to the apparatus in the desired amounts and their pressures read on a McLeod gage. The method of purifying and admitting the gases to the resonance vessel was the same as that described by Mitchell

¹ Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926).

and Dickinson.² Light from a quartz mercury arc, cooled by water at a definite temperature, was allowed to shine on the quartz window of the resonance vessel. In some cases a light filter consisting of a quartz cell containing 3 mm. thickness of a 25% solution of acetic acid was used. This filter was found to cut out radiation below 2400 Å., which was shown¹ to decompose ammonia photochemically, giving rise to hydrogen as a product. As the amount of hydrogen formed per unit time in the direct photochemical decomposition was known to be several times as great as the amount formed in the sensitized decomposition, it was thought necessary to use the filter. However, on account of the intensity of the light (distance from the window 10 cm.) and the short time of exposure, very little decomposition took place. One experiment made using no filter (see Fig. 2) gave substantially the same results as when the filter was used. The filter was only used in cases where relative intensities were desired, except in the above-mentioned case. A small Hilger quartz prism spectrograph was used for photographing the ultraviolet band.

In cases where intensity measurements were desired, calibration spots were placed on the plate by exposing portions of it to light from a small flash light bulb at different distances for the same length of time used in the fluorescence exposures (1 minute). The plates were measured on a microphotometer and the galvanometer deflections plotted against the square of the distance to the light. The relative intensities of the bands were obtained by recording the minimum galvanometer deflections (corresponding to the maximum of intensity of the band) and reading off the intensities from the plot. A small correction for the blackening of the plate in the region from 3180 to 3650 Å., due to scattered light from the window, was made by subtracting the intensity at zero ammonia pressure from each of the intensities at higher pressures.

Experimental Results

With 7 mm. of ammonia in the vessel, the green fluorescence was observed and photographs showed the diffuse bands stretching from 3170 to 3650 Å., with a maximum around 3370 Å.

Experiments made with the same pressure of nitrogen showed green fluorescence but photographs showed no ultraviolet band. The plate showed, incidentally, a line or perhaps a band-head at about 3370 Å., near the mercury line 3342 Å. which was reflected from the quartz window.

Experiments made with 7 mm. of argon, 40 mm. of argon and 7 mm. of hydrogen showed neither green nor ultraviolet bands. Indeed nothing was visible on the plate except the mercury lines reflected from the window, the fluorescent band of quartz between 4046 and 4358 Å., and the 2537 Å. resonance line of mercury.

² Mitchell and Dickinson, *THIS JOURNAL*, **49**, 1478 (1927).

Photographs with an uncooled arc and ammonia showed neither green nor ultraviolet bands.

Photographs were taken with different ammonia pressures in the vessel, using the cooled arc, and the plates were photometered. The relative intensities of the ultraviolet band were plotted against the pressures of ammonia as shown in Fig. 1. On Fig. 1 are also plotted rates of decomposition of ammonia, in arbitrary units, as a function of the ammonia pressure.

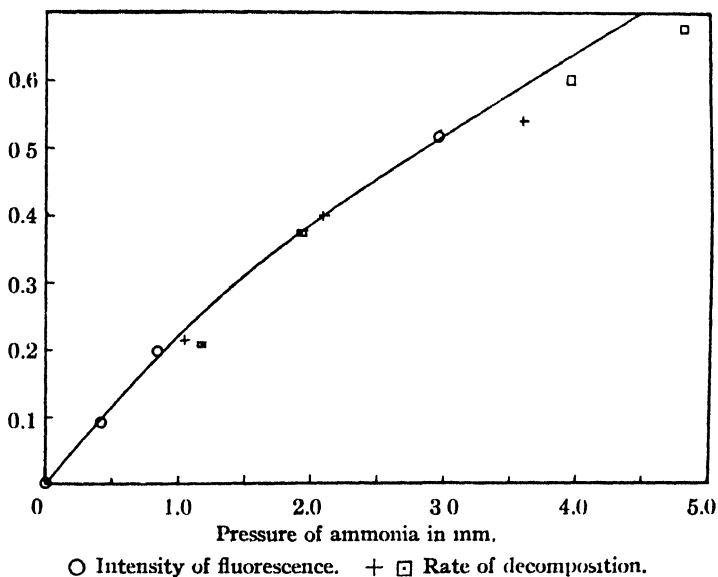


Fig. 1.

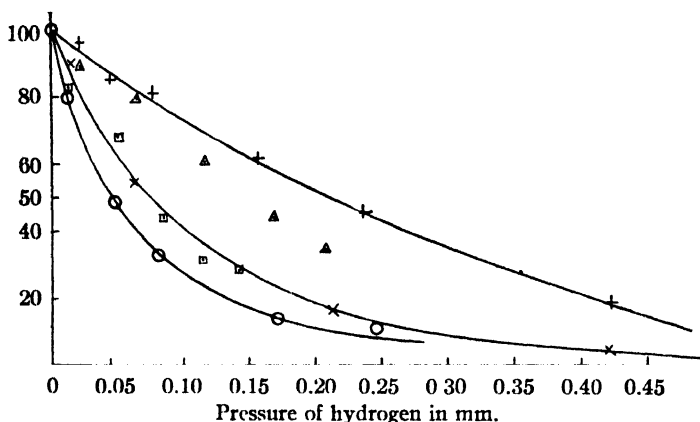
Finally, experiments were made in which a constant pressure of ammonia was kept in the vessel and various amounts of hydrogen were added. Small amounts of hydrogen were found to decrease the intensity of the ultraviolet band to a marked degree. The plates were photometered and the results are shown in Fig. 2. Relative intensities are plotted as ordinates against pressure of hydrogen as abscissas for three different ammonia pressures, namely, 5.04 mm., 3.00 mm. and 2.82 mm. Fig. 2 also contains results of experiments on the effect of hydrogen on the rate of sensitized decomposition of ammonia.²

Discussion of Results

The above experiments show that mercury atoms, excited by the absorption of the resonance line 2537 Å. of mercury, are necessary for the production of the ultraviolet and green bands, since no bands were observable when the lamp was run hot so that the center of the line was reversed. Confining our attention to the ultraviolet band for the moment,

the experiments show that this band occurs when ammonia is present. Hence, ammonia and mercury atoms in the 2^3P_1 or 2^3P_0 states are necessary for the production of the band.

It will be seen from Fig. 1 that the dependence of the intensity of fluorescence on the pressure of ammonia agrees quite well with the dependence of the rate of sensitized decomposition on ammonia pressure. The possibility of so adjusting the scale of ordinates that the fluorescence and the rate curves coincide shows that there is a proportionality between the intensity of fluorescence and the rate of decomposition of ammonia. The proportionality between the intensity of fluorescence and the rate of sensi-



+ Quenching of fluorescence, $P_{\text{NH}_3} = 5.04$ mm.; \circ Quenching of fluorescence, $P_{\text{NH}_3} = 2.82$ mm.; \times Quenching of fluorescence (no filter), $P_{\text{NH}_3} = 3.0$ mm.; \triangle Rate of decomposition, $P_{\text{NH}_3} = 5.06$ mm.; \square Rate of decomposition, $P_{\text{NH}_3} = 3.22$ mm.

Fig. 2.

tized decomposition can be accounted for on the assumption that excited ammonia molecules are responsible for both the fluorescence and the decomposition.

From Fig. 2 it will be seen that small amounts of hydrogen have a marked effect in decreasing the fluorescence and that the relative effect is greater, the smaller the ammonia pressure. If the sole role of the hydrogen were to take activation from the mercury atoms, we should expect that at very low pressures of ammonia the amount of hydrogen necessary to decrease the intensity of fluorescence to one-half would be the same as that necessary to decrease the resonance radiation of mercury by the same amount. This pressure of hydrogen was shown by Stuart³ to be 0.2 mm. However, from Fig. 2 it is to be noticed that at pressures of ammonia as high as 3 mm. only 0.05 mm. of hydrogen is necessary to decrease the intensity of the

³ Stuart, *Z. Physik*, **32**, 262 (1925).

fluorescence to one-half. The proportionality between the intensity of fluorescence and the rate of sensitized decomposition is even more striking in Fig. 2, since the curves there show considerably more curvature than those of Fig. 1. The explanation of the large effect of hydrogen on the rate of decomposition, that hydrogen can take activation from excited ammonia molecules by collision of the second kind, is applicable to the intensity of fluorescence if ammonia be assumed to be the emitter.

Rayleigh⁴ and Houtermans⁵ have found that diffuse bands are emitted by distilling mercury vapor which has been radiated by the light from a cooled quartz mercury arc. One band, with a maximum at 3370 Å., bears a striking similarity to the band described in this paper; however, another band occurs at 2539 Å., which is not observed in mixtures of ammonia and mercury. If it is assumed that the 3370 Å. band from boiling mercury is identical with that from mercury-ammonia mixtures it becomes difficult to explain the above facts, since it is not easy to see how the fluorescence would then depend on the pressures of ammonia and hydrogen in the way it does. In particular it is difficult to see how the explanation given by Houtermans for the bands in distilling mercury vapor could be made to fit the facts observed in the case of the fluorescence of mercury and ammonia at room temperature. However, the dependence of the intensity of fluorescence on the pressure of ammonia and hydrogen is readily explained on the assumption that the emitter is an ammonia molecule which has been activated by collision of the second kind with an excited mercury atom.

The writer wishes to express his thanks to Dr. R. G. Dickinson for his advice and interest in this work, and to Mr. F. Petit of the Mount Wilson Observatory for the use of a microphotometer. Financial assistance has been received from the Carnegie Institution of Washington through a grant to Professor A. A. Noyes.

Summary

The intensity of the diffuse band, with a maximum at 3370 Å., emitted when mixtures of ammonia and mercury vapor at room temperature are irradiated with mercury resonance radiation 2537 Å., has been found to vary with ammonia and hydrogen pressures in the same manner as the rate of sensitized decomposition of ammonia. It is suggested that excited ammonia molecules are responsible for both emission and decomposition.

PASADENA, CALIFORNIA

⁴ Rayleigh, *Proc. Roy. Soc. (London)*, **111**, 456 (1926).

⁵ Houtermans, *Z. Physik*, **41**, 140 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE SURFACE TENSION OF LIQUID CARBON DIOXIDE

BY ELTON L. QUINN

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Interest in the question of solubility led the author a few years ago to inquire whether liquids which exist only under very high pressures behave in the same manner towards solutes as those with which we are most familiar. The answer to this inquiry was not easy to obtain from the literature because of the small amount of quantitative work which has been done on such liquids. It seemed worth while, therefore, to attempt to determine some of the important properties of a liquid of this type and, if possible, to fit it into the solubility theory of Hildebrand.¹ As carbon dioxide exists as a liquid at ordinary temperatures only under very high pressures and under these conditions is but slightly removed from its critical temperature, it may well be used for determinations of this kind.

One of the most useful properties of a liquid, which can be used for calculating its internal pressure and therefore its position in a solubility table, is its surface tension. Although a few surface tension measurements have been made on liquid carbon dioxide² it cannot be said that these values are reliable enough or extensive enough to be used as a basis for such a calculation. The work described in this paper was carried out in an attempt to obtain enough data to predict some of the solubility relations of this compound. Later, if possible, these results will be checked against some actual solubility determinations.

On account of the extremely high vapor pressure of carbon dioxide at ordinary temperatures, the capillary tube method is the only one that can be readily applied to the solution of this problem. The pressure of its saturated vapor at 20° is about 56 atmospheres and therefore the apparatus must be designed for strength, which will, of course, render it difficult to apply all the refinements which are usually applied to measurements of this kind.³

Preparation of Tubes

Capillary tubes were made by drawing down ordinary soft glass tubes to a diameter of about 0.2 to 0.5 mm. Selected pieces from a very large number of these tubes were inspected with a microscope for uniformity of bore and circular cross section. The tubes which passed this inspection were then placed in carefully cleaned Pyrex glass tubes of 1 cm. internal diameter which had been sealed at one end. They were fitted with small platinum wires placed in such a way that the capillary was held firmly in the center of the tube. The Pyrex tubes were then constricted just above the end of the

¹ Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York City, 1924.

² Verschaefelt, *Verhandel, Akad. Wetenschappen Amsterdam*, 4, 74 (1895).

³ Richards and Coombs, *THIS JOURNAL*, 37, 1656 (1915).

capillary to facilitate the final sealing. The tubes when finished were about 15 cm. in length.

The carbon dioxide used for filling the Pyrex tubes as well as that used for making the freezing mixtures was furnished through the courtesy of the Carbo Chemical Company of Salt Lake City. The analysis of the gas from the top of the cylinder showed it to be 99.8% carbon dioxide; this value increased somewhat as the gas was drawn from the cylinder. There was no evidence of oil but there was a small amount of water vapor in the gas. A long drying tube filled with calcium chloride was connected at one end with the carbon dioxide cylinder and at the other with the Pyrex tube containing the capillary. These connections were made with small copper tubing and the joint between the copper tube and the glass tube was made with de Khotinsky cement. The glass tube was placed in a freezing mixture of carbon dioxide snow and ether and the liquid carbon dioxide distilled from the standard carbon dioxide cylinder into it. The freezing mixture was easily kept at -100° by reducing the pressure of the carbon dioxide above it with a vacuum pump. After the glass tube had been purged several times with carbon dioxide to remove all of the air, it was partly filled with liquid and allowed to stand until the carbon dioxide had frozen to a transparent mass. It was then sealed in an oxy-gas flame at the constriction and the contents were allowed to melt.

Eight tubes were prepared in the above manner and used for several months without breaking. This was quite remarkable as several tubes of much thicker sodium glass exploded in the preliminary trials.

Temperature Control

Fig. 1 is a drawing of the thermostat in which the tubes were placed for measurement. *A* is an inverted standard 20-lb. carbon dioxide cylinder containing the liquid carbon dioxide. It was connected through the needle valve *B* with the coil of copper tubing placed in the unsilvered vacuum tube *C*. This vacuum tube was about 9 cm. in diameter by about 30 cm. high. It was

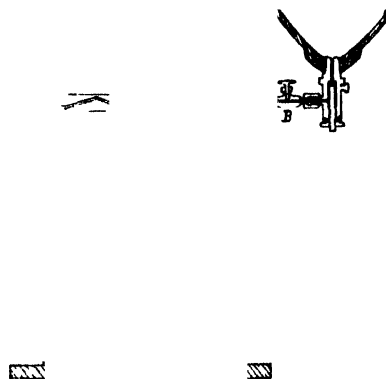


Fig. 1.

placed in a wooden box in which it just fitted. This box was then placed in a larger one, leaving a space of about two inches all around which was then packed with mineral wool. Two windows, indicated in the drawing by the dotted lines, were placed opposite each other in order to make it possible to observe the contents of the tube. The bath liquid was alcohol and this was kept in constant agitation by means of the brass pump *E*. This pump was essentially an air-lift pump and the com-

pressed air, which had been pre-cooled, forced the alcohol up the tube and forced it out at the top of the bath. The cooling of the air took place in the apparatus marked *D*, which in this case was a coiled glass tube around which the escaping carbon dioxide from the bath was allowed to pass. With this apparatus it was possible to lower the temperature of the bath to -50° and with close attention to keep it constant to within $\pm 0.2^{\circ}$. The temperature was changed by manipulating the needle valve *B*, and as one temperature was not needed longer than about three hours at a time this did not prove to be very troublesome.

Temperatures were measured with a pentane thermometer which had been calibrated by the Bureau of Standards and was checked again just before this work was started. The freezing points of water and mercury and the sublimation temperature of solid carbon dioxide were taken as the fixed points.

The capillary rise of the carbon dioxide was measured with a cathetometer. It so happened that the micrometer screw of this cathetometer was long enough to measure the greatest height of the liquid without making necessary any other adjustments of the instrument. Four tubes were used at each temperature and at least five readings of the cathetometer were made on each tube, the observed heights h_0 given in Table II being the average of these readings.

At each temperature where readings were taken the height of the meniscus in the capillary tube was measured with a meter stick. This was done to determine the point at which the capillary should be cut for measuring its diameter. This point was very nearly constant for all temperatures, in no case varying more than 5 mm. The capillary was cut at the average of these heights, each piece set in a paraffin block, the cut ends colored with drawing ink and the diameter measured with a microscope fitted with a micrometer attachment with movable cross hairs. One graduation mark on this micrometer screw head was equal to 0.0006 mm. but probably the error of setting the cross hairs was great enough so that the individual measurements were not accurate to within ± 0.005 mm. Five measurements were made on each piece of the capillary in each of two directions, which were at right angles to each other, and the average of these twenty measurements was taken as the inner diameter of the tube.

Calculations

The observed height h_0 was corrected for the quantity of liquid in the meniscus by means of the equation $h_1 = h_0 + r/3$, where h_1 is the corrected height and r the radius of the capillary. Although this equation is not exact, it was found by Richards and Carver⁴ to apply with sufficient accuracy where the value of r is small, as it is in this case.

⁴ Richards and Carver, *THIS JOURNAL*, 43, 828 (1921).

The surface tension was calculated by means of the equation $\gamma = \frac{1}{2} rhg(D - d)$, where γ is the surface tension in dynes per centimeter, g the acceleration due to gravity, which at Salt Lake City is 979.8 cm./sec.²; D is the density of the liquid carbon dioxide, and d the density of the saturated vapor. The values for these gas densities between 0° and the critical temperature (31.35°) were taken from Amagat's table.⁵ By plotting the values for the density of liquid carbon dioxide obtained by Behn⁶ and those obtained by Jenkin⁷ on large scale cross-section paper, a curve was obtained which served very well to indicate the liquid densities down to -60°. The values obtained by Amagat above 0° gave a satisfactory agreement with those read from this curve. The only determinations we have of the density of the saturated vapor of carbon dioxide below 0° were made by Cailletet and Mathias.⁸ We have in addition to these determinations some calculated values by Jenkin⁹ and some extrapolated values calculated by Mollier by means of Amagat's values above 0°.¹⁰ On account of the general acceptance of Amagat's values above 0°, it seemed best to make a new extrapolation of his curve to temperatures below zero in order to obtain the data necessary for making the surface tension calculations. This extrapolation was carried out by first plotting the experimental values of Amagat against the temperature and drawing the curve. The equation of this curve was found to be $Td = 1.936 P^n$, which can be readily derived from the gas laws if we keep in mind that in the case of an actual gas $P^n V = K$.¹¹ In this equation, d is the density of the saturated vapor, T the temperature in degrees absolute, 1.936 is a constant, P is the vapor pressure in atmospheres and the exponent n is equal to $0.737 + 0.0048t$, where t is the temperature in degrees centigrade. The values for P for the vapor pressure of liquid carbon dioxide were taken from the tables in Landolt-Börnstein.¹² Table I shows the agreement between the densities calculated by means of this equation and the observed experimental results.

Richards and Coombs showed that a considerable error is introduced when a capillary tube is set in a narrow outer jacket. They found that in the case of water the outside tube must be greater than 38 mm. in order to make this correction negligible. From the experience the author has had using large quantities of liquid carbon dioxide in glass tubes it seemed quite unsafe to use an outer jacket larger than 1 cm. in internal

⁵ Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893).

⁶ Behn, *Ann. Physik*, [4] 3, 733 (1900).

⁷ Jenkin, *Proc. Roy. Soc. (London)*, 98A, 170 (1920).

⁸ Cailletet and Mathias, *J. Phys.*, [2] 5, 549 (1886).

⁹ Jenkin, *Trans. Roy. Soc. (London)*, 213A, 67 (1914).

¹⁰ Mollier, *Z. ges. Kälte-Ind.*, Nos. 4 and 5, 66 and 85 (1895).

¹¹ Leinweber, *Z. Ver. deut. Ing.*, 60, 363-6 (1916).

¹² Landolt-Börnstein-Roth-Scheel, "Physikalisch-Chemische Tabellen," p. 1342.

TABLE I

CALCULATED AND OBSERVED VALUES FOR THE DENSITY OF THE SATURATED VAPOR OF CARBON DIOXIDE FROM 25 TO -29.8°

Temp., $^{\circ}\text{C}.$	Density, obs.	Observer	Density, calcd.	Diff.
25	0.240	Amagat	0.227	-0.013
20	.190	Amagat	.190	.000
15	.158	Amagat	.159	+ .001
10	.133	Amagat	.134	+ .001
5	.114	Amagat	.113	- .001
0	.096	Amagat	.096	.000
-12	.069	Cailletet	.067	- .002
-21.8	.052	Cailletet	.049	- .003
-29.8	.035	Cailletet	.032	- .003

diameter. It became necessary, therefore, to apply a correction to each reading for the capillary effect of the outside tube. The internal diameter of the eight outer jackets used averaged 0.96 cm., with a variation of only 0.01 cm. All of the capillary tubes had an outside diameter of 0.1 cm. The effect of this capillary was to decrease the diameter of the outside tube, so this value was subtracted from 0.96, giving 0.43 as the value of the radius of the outside jacket. The corrections were calculated by means of the equation $h = h_1 r / 0.43$, where h is the correction to be added to the observed height, h_1 the observed height and r the radius of the capillary. While the correction for each tube is indicated in the table, only the average of these values at each temperature was added to the observed height.

The results of these measurements and calculations are tabulated in Table II.

TABLE II

SURFACE TENSION MEASUREMENTS OF LIQUID CARBON DIOXIDE

Temp., $^{\circ}\text{C}.$	Tube no.	Obs. height, h_0 , cm.	Corr. height, h_1 , cm.	Correction for capillary effect of outer jacket, cm.	Corr. height, h_2 , cm.	Density of liquid D	Density of vapor d	$D - d$	Surface tension γ , dynes per cm.	Average value of γ
25	1	0.133	0.139	0.006	0.145	0.703	0.240	0.463	0.59	0.59 (not averaged)
	2	.141	.147	.006	.153	.703	.240	.463	.69	
	3	.178	.182	.006	.188	.703	.240	.463	.59	
20	1	.252	.258	.011	.269	.766	.190	.576	1.37	1.37
	2	.242	.248	.011	.259	.766	.190	.576	1.44	
	3	.317	.321	.010	.332	.766	.190	.576	1.30	
	4	.199	.206	.011	.217	.766	.190	.576	1.37	
15	1	.345	.351	.015	.365	.814	.158	.656	2.12	2.09
	2	.316	.322	.015	.336	.814	.158	.656	2.14	
	3	.434	.438	.014	.452	.814	.158	.656	2.02	
	4	.269	.276	.014	.290	.814	.158	.656	2.10	
10	1	.444	.450	.019	.468	.856	.133	.723	2.00	2.94
	2	.394	.400	.018	.418	.856	.133	.723	2.93	
	3	.554	.558	.018	.576	.856	.133	.723	2.84	
	4	.340	.347	.018	.365	.856	.133	.723	2.91	

TABLE II (Concluded)

Temp., °C.	Tube no.	Obs. height, h_0 , cm.	Corr. height, h_1 , cm.	Correc- tion for capillary effect of outer jacket, cm.	Corr. height, h_2 , cm.	Density of liquid D	Density of vapor d	$D - d$	Surface tension γ , dynes per cm.	Ave- rage value of γ
5	1	.526	.532	.022	.554	.888	.114	.774	3.80	3.75
	2	.487	.493	.023	.515	.888	.114	.774	3.86	
	3	.662	.666	.022	.688	.888	.114	.774	3.63	
	4	.403	.410	.021	.432	.888	.114	.774	3.69	
0	1	.610	.616	.026	.642	.914	.096	.818	4.66	4.62
	2	.570	.576	.027	.602	.914	.096	.818	4.77	
	3	.767	.771	.025	.797	.914	.096	.818	4.44	
	4	.480	.487	.025	.513	.914	.096	.818	4.62	
- 6	1	.716	.722	.030	.752	.960	.080	.880	5.87	5.79
	3	.919	.923	.030	.953	.960	.080	.880	5.71	
-11.3	5	1.540	1.543	.033	1.577	.987	.067	.920	6.54	6.81
	6	1.071	1.075	.034	1.109	.987	.067	.920	6.80	
	7	0.861	0.867	.034	.901	.987	.067	.920	6.90	
	8	.913	.919	.034	.953	.987	.067	.920	7.00	
-21.7	5	1.934	1.937	.041	1.979	1.037	.049	.988	8.81	9.05
	6	1.285	1.289	.041	1.331	1.037	.049	.988	8.76	
	7	1.083	1.089	.043	1.131	1.037	.049	.988	9.30	
	8	1.135	1.141	.042	1.183	1.037	.049	.988	9.33	
-32.3	5	2.276	2.279	.049	2.328	1.084	.036	1.048	11.00	11.25
	6	1.603	1.607	.051	1.656	1.084	.036	1.048	11.50	
	7	1.247	1.253	.049	1.302	1.084	.036	1.048	11.36	
	8	1.277	1.283	.048	1.332	1.084	.036	1.048	11.14	
-42.7	5	2.734	2.737	.059	2.795	126	.027	1.099	13.84	13.88
	6	1.844	1.848	.058	1.906	126	.027	1.099	13.95	
	7	1.468	1.474	.058	1.532	126	.027	1.099	14.02	
	8	1.497	1.503	.057	1.561	126	.027	1.099	13.70	
-52.2	5	3.070	3.073	.066	3.139	168	.019	1.149	16.25	16.54
	6	2.096	2.100	.066	2.166	168	.019	1.149	16.58	
	7	1.676	1.682	.066	1.748	168	.019	1.149	16.72	
	8	1.740	1.746	.065	1.812	1.168	.019	1.149	16.62	

Internal Diameter of Capillary Tubes

Tube no.	1	2	3	4	5	6	7	8
Diameter, cm.	0.0363	0.0397	0.0278	0.0450	0.0184	0.0272	0.0341	0.0326

Discussion of Results

It is interesting to apply the above results to the equation of de Block¹³ which he writes in the following form, $\gamma = K(t_c - t)^n$; where t_c is the critical temperature of the liquid; γ is the surface tension at the temperature t in degrees centigrade; $K = \gamma_0/(t)^n$; γ_0 is the surface tension at 0° ; and the exponent n is approximately 1.2 for all non-polar liquids. The average value for n , which is not exactly constant over the range of temperatures used, is 1.24 for carbon dioxide. In order to get this value for n it is necessary to take 4.68 for the surface tension at 0° instead of 4.62 as given in Table II. This is justified by the fact that 4.68 at 0° falls exactly on the surface-tension curve made by plotting the above values on cross-section paper; also if we do not include the lowest value obtained at 0° in our average we get a value of 4.68 dynes per centimeter.

¹³ De Block, *Bull. sci. acad. roy. Belg.*, [5] 11, 292-300, 353-60 (1925).

We can now rewrite the de Block equation so that in the case of carbon dioxide it becomes $\gamma = .0653(31.35 - t)^{1.24}$. Table III shows the agreement between the observed and calculated values for the surface tension at various temperatures. The calculated values were obtained from the above equation. The values of n in the second column were obtained by substituting the experimental surface-tension values in the de Block equation and solving for n .

TABLE III

SHOWING THE AGREEMENT BETWEEN THE OBSERVED AND CALCULATED VALUES FOR THE SURFACE TENSION OF LIQUID CARBON DIOXIDE

Temp., °C.	n	γ , obs.	γ , calcd.	Diff.
20	1.21	1.37	1.33	-0.04
10	1.21	2.94	2.90	- .04
5	1.27	3.75	3.77	+ .02
- 6	1.21	5.79	5.81	+ .02
-11.3	1.22	6.81	6.85	+ .04
-21.7	1.25	9.05	8.99	- .06
-32.3	1.24	11.25	11.26	+ .01
-42.7	1.26	13.88	13.59	- .29
-52.2	1.29	16.54	15.77	- .77

There are several ways of treating surface tension measurements to determine the internal pressure of a liquid.¹⁴ Perhaps one of the most convenient methods in this case is to calculate its total energy of surface formation E_s by means of the Thomson equation, $E_s = \gamma - Td\gamma/dT$. At 20° E_s becomes 61.9 when $d\gamma/dT$ is taken over the whole temperature range studied. This places carbon dioxide with carbon tetrachloride, toluene and chloroform in the Hildebrand series and indicates that it should behave as a solvent much as these liquids do. This cannot be confirmed by experimental evidence, as no measurements have been made on the solubility of these substances in liquid carbon dioxide. We know, however, that carbon dioxide in the solid state is readily soluble in ethyl ether¹⁵ and must have, therefore, nearly the same internal pressure. As ethyl ether is only slightly removed from these compounds in the internal pressure series, we may safely assume that they would behave in much the same manner towards carbon dioxide.

The author expects to treat this question of solubility more fully in a later communication.

The author wishes to acknowledge with gratitude the suggestions which Dr. J. H. Hildebrand made at the beginning of this work.

Summary

1. An equation has been derived for calculating the density of the saturated vapor of carbon dioxide from 25 to 0°. This equation gives

¹⁴ Ref. 1, p. 111.

¹⁵ Thiel and Schulte, *Z. physik. Chem.*, **96**, 312 (1920).

values which agree very well with the observed densities over this range. Use was made of this equation to calculate densities down to -52.2° .

2. Surface-tension measurements of liquid carbon dioxide have been made from 25 to -52.2° .

3. The equation of de Block when put into the form $\gamma = .0653(31.35 - t)^{1.24}$ was found to fit the experimental results for the surface tension of carbon dioxide very well except at lower temperatures.

4. From its total energy of surface formation it was found that carbon dioxide had an internal pressure about the same as carbon tetrachloride, toluene and chloroform.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE EFFECT OF IRON AND OXYGEN ON THE ELECTRICAL CONDUCTIVITY OF COPPER¹

BY RUSSELL P. HEUER

RECEIVED JUNE 18, 1927

PUBLISHED NOVEMBER 5, 1927

The electrical conductivity of dilute solid solutions of metallic elements in copper has been the subject of many investigations. The data presented treat the binary systems of copper and practically every metal which may occur as an impurity in commercial copper, namely, silver, gold, zinc, cadmium, aluminum, tin, phosphorus, arsenic, antimony, iron, cobalt and nickel.² Unfortunately much discordance is evident in the published results.

In illustration, the solute element iron may be considered. Addicks³ in his pioneer work upon the impurities of copper attempted to evaluate the effect of the 0.002 to 0.005% of iron present in electrolytic copper. From measurements upon alloys of 0.042, 0.046 and 0.068% of iron and upon pure copper, he interpolated for intermediate iron concentrations and concluded that the conductivity was lowered at the rate of 140% of the International Standard value for each 1% of iron present.

Hanson and Ford⁴ at the National Physical Laboratory in England, under Rosenhain's direction, have recently repeated Addicks' work, extending the data to higher iron concentrations. Using the observed conductivity of an alloy of 0.2% of iron, they project a curve to pure copper and suggest a lowering in conductivity at the rate of 235% for 1% of iron.

¹ A thesis for the degree of Doctor of Philosophy, presented to the Graduate Faculty of the University of Pennsylvania.

² Guertler, "Handbuch der Metallographic," Berlin, 1925; Circular No. 73, Copper, U. S. Bureau of Standards, 1922.

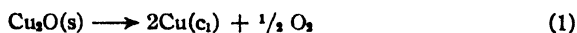
³ Addicks, *Trans. Am. Inst. Min. Eng.*, **36**, 18 (1906).

⁴ Hanson and Ford, *J. Inst. Metals*, **32**, 335 (1924).

They measured one alloy in this interpolated range. It contained 0.06% of iron. Curiously its conductivity was only about 1% lower than their value for pure copper. Such high conductivity is a considerable deviation from the established behavior of solid solutions. It indicates that the iron in the 0.06% alloy was not present in solid solution.

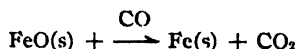
In an effort, perhaps, to simulate commercial copper, Addicks' and Hanson's alloys all contained cuprous oxide as a soluble component of the liquid phase. The assumption is made in their work that the effect of this oxide is negligible or at least is constant while they perform the interpolation between iron of zero concentration and iron at the measured concentration.

Thermodynamic consideration of the ternary system copper-iron-oxygen shows such assumption to be incorrect. Cuprous oxide is thermally dissociated. Roberts and Smyth⁵ measured the equilibrium pressure of liquid copper saturated with cuprous oxide. For the reaction



they record the data: 1392.3°K. = 0.028 mm. of Hg, 1423.5°K. = 0.035 mm. of Hg; 1457.1°K. = 0.041 mm. of Hg. Selecting solid cuprous oxide and pure liquid copper as the states of unit activity and assuming the activity of copper to equal its mole fraction, the above reaction can be evaluated for ΔF° at 1398°K. and 1336°K. These temperatures are chosen to be, respectively, the temperature of formation of the liquid alloy and the eutectic temperature of the copper-cuprous oxide system. $\Delta F^\circ_{1398} = +17,490$ cal.; $\Delta F^\circ_{1336} = +17,430$ cal.

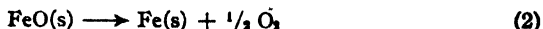
Eastman⁶ has examined critically the recorded data for equilibrium in the reaction



Using Lewis and Randall's⁷ value of ΔF° for the reaction

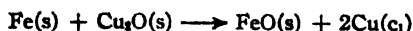


he evaluates ΔF° for the reaction



for temperatures of 100° intervals from 873 to 1273°K. Extrapolating slightly, $\Delta F^\circ_{1398} = +41,295$ cal.; $\Delta F^\circ_{1336} = +42,260$ cal.

Combining Equations (1) and (2) to obtain the reaction



$\Delta F^\circ_{1398} = -23,805$ cal.; $\Delta F^\circ_{1336} = -24,830$ cal.

Assuming the insolubility of ferrous oxide in molten copper and utilizing

⁵ Roberts and Smyth, *THIS JOURNAL*, **43**, 1061 (1921).

⁶ Eastman, *ibid.*, **44**, 875 (1922).

⁷ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

the fact that at the eutectic temperature the activity of cuprous oxide becomes unity, the equilibria are expressed

$$\text{at } 1336^{\circ}\text{K. } a_{\text{Fe}} = 8 \times 10^{-5} \quad (3)$$

$$\text{at } 1398^{\circ}\text{K. } a_{\text{Fe}} \times a_{\text{Cu}_2\text{O}} = 19 \times 10^{-5} \quad (4)$$

Equation (4) defines a curve, abc, in Fig. 1 which limits the composition of the ternary alloys which can exist at 1125° . Alloys of composition *M* react to eliminate FeO and arrive at the composition *R*, with very small oxygen content. Alloys of composition *N* react similarly to reach *S*, the equilibrium composition containing little residual iron.

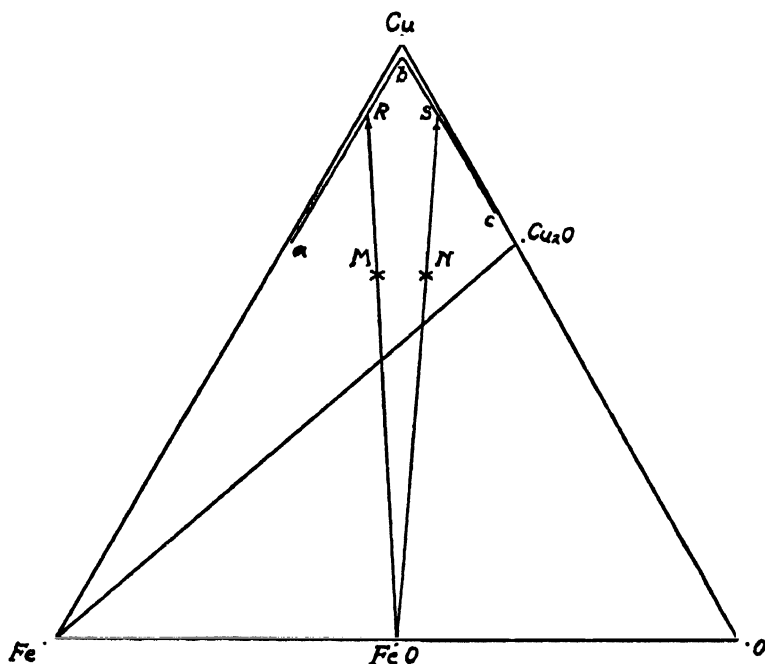


Fig. 1.

Equation (3) defines a line of constant activity, such as TU in Fig. 2, which at 1063° divides the ternary diagram into two areas. Within TUV, iron and eutectic cuprous oxide react, forming ferrous oxide until the iron is reduced to the equilibrium activity 8×10^{-5} or the cuprous oxide phase is consumed. Only within the small area TUVZ can iron and cuprous oxide pass through the eutectic temperature without reacting.

In the absence of data relating the activity of iron and cuprous oxide in copper solutions to the mole fractions, these equilibrium concentrations cannot be calculated. We know, however, that these solutes exhibit quite low solubility in copper. The iron activity in such case doubtless exceeds its mole fraction. The line TU lies, therefore, at or less than 0.008% of iron.

This indicates the presence of indefinite amounts of ferrous oxide in Addicks' and Hanson's alloys. The application of their data to the conductivity of the system copper-iron is thus open to objection.

The present work is planned to take the effect of oxygen into consideration. The alloys are based upon the ternary system copper-iron-oxygen. The copper-rich alloys of the binary systems copper-iron and copper-oxygen are measured. The ternary alloys are then investigated and the lines abc and TU located.

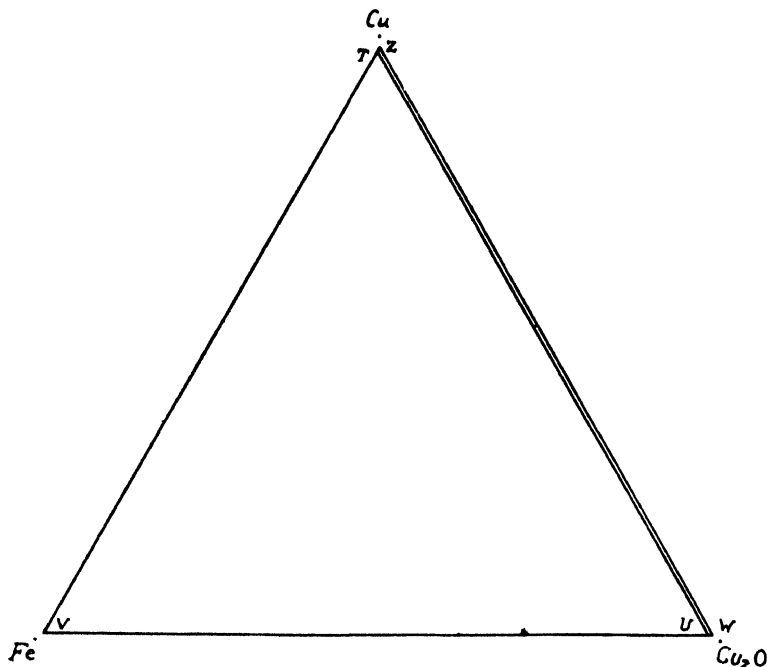


Fig. 2.

Experimental

Pure copper for the alloys was prepared by two successive electrolytic depositions of the metal. Pure electrolyte free of metallic impurities was used in the final deposition. The cathodes analyzed: Ag, 0.0003%; As, 0.0000%; Sb, 0.0001%; Bi, 0.0000%; Fe, 0.0001%; Co, 0.0000%; Ni, 0.0001%; Zn, 0.0000%; Pb, 0.0000%; S, 0.0004%; Se + Te, 0.0000%.

The melts were prepared in a platinum resistance furnace having a vertical heating chamber 12 inches high and 3 inches in diameter. The furnace was evacuated and filled with dry, oxygen-free nitrogen. The system of crucibles and feeders used is shown in Fig. 3. For the binary series copper-iron, electrolytic iron chips to form the desired alloy were placed in the thimble (b). The feeder (a) contained 375 g. of copper and 300 g. of anhydrous barium chloride. Seven hours were required for making each

melt, three and one-fourth hours for heating to 1125° , three-fourths of an hour at that temperature and four hours for slow cooling. Practically all the cuprous oxide was removed from the liquid metal by the solvent action of the molten barium chloride.

The solidified melts were sampled for metallographic specimens and forged hot to a $\frac{5}{8}$ -inch octagon section. Scale and surface defects were removed by machining to $\frac{9}{16}$ -inch diameter, whereupon the samples were annealed to 950° for fifty hours in carbon dioxide and cooled slowly to equalize any cored structure present in the original dendrites. The forgings were then drawn cold to 12 gage (0.080 inch diameter) wire and annealed at 500° by passing an electric current through the wire. The conductivity was measured at 20° with an accuracy of 0.1%, using the standard bridge; 0.15328 ohms per meter gram was considered 100% conductivity.

Chemical analyses for copper, oxygen, sulfur and iron were made on each melt. Copper was determined on turnings removed from the cast piece. Two 10g. electrolytic assays were made, checking within 0.003%. Oxygen and sulfur were determined by ignition in hydrogen at 900° to convert these elements to water and hydrogen sulfide.* The sulfide evolved was absorbed in ammoniacal cadmium chloride solution and evaluated by iodine titration. The loss in weight of the sample upon this ignition was attributed to oxygen and sulfur. Knowing the sulfur value, oxygen was determined by difference.

Sixty g. of wire samples from the conductivity measurements were used in this analysis. After cleaning the metal surface, as recommended, with abrasive, dilute alcoholic potassium hydrate, dilute potassium cyanide, distilled water, alcohol and ether, there was no assurance that upon drying at 80° the surface would be free of oxide or adsorbed substances. That adsorbed substances were present seemed proved when metal so prepared was ignited in carbon dioxide and lost 0.0008% in weight. Since all material volatile in carbon dioxide from within the copper had been removed by previous annealing at 950° for fifty hours, this loss must have been a surface effect. Upon further ignition in hydrogen at 900° for five hours, this piece lost 0.0006% as oxygen. Some of this might have been surface oxygen. To overcome these surface effects, a similar sample was given a rapid preliminary heating in hydrogen to 550° , held for three minutes and cooled rapidly. This freed the adsorbed material and removed surface oxygen. Upon further treatment at 900° for five hours, 0.0004% of oxygen was lost. From this the preliminary hydrogen heating was considered more satisfactory than ether drying and carbon dioxide ignition, where such small amounts of oxygen were involved. Iron was determined on the conductivity samples, after electrolytically removing the copper, by double precipitation with gaseous ammonia and weighing as ferric oxide.

It was found impossible to use the crucible assembly shown in Fig. 3 for making copper free of iron, due to a considerable "pick-up" of iron from the crucible. To overcome this, a silica tube ten inches long and seven-eighths of an inch inside diameter, sealed at one end, was substituted for the crucibles. Two hundred g. of copper and 75 g. of barium chloride were charged. The copper used was specially freed from sulfur

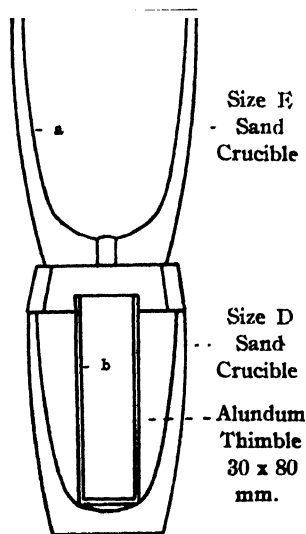


Fig. 3.—Crucible assembly.

* Bassett and Bedworth, *Trans. Am. Inst. Mining Met. Eng.*, 73, 784 (1926).

by ignition in hydrogen. The melt piped badly but sufficient metal for one conductivity measurement was obtained.

For the binary series copper-cuprous oxide, methods similar to those employed for the copper-iron series were used. The charge, of course, contained no iron addition and no barium chloride. The oxygen addition was made by allowing the desired amount of oxygen gas to be present in the nitrogen atmosphere of the furnace. No annealing of the forged pieces for fifty hours at 950° was required. In the oxygen determination, ether drying at 80° was used for the preparation of the sample.

For the ternary alloys, the methods of the copper-cuprous oxide series were adopted. A copper-iron alloy containing 2.2% of iron was used for the iron addition. The amount desired was charged in the feeder crucible.

Results

The data for the binary system copper-iron are assembled in Table I. Fig. 4 expresses the relation of conductivity to atomic per cent. of

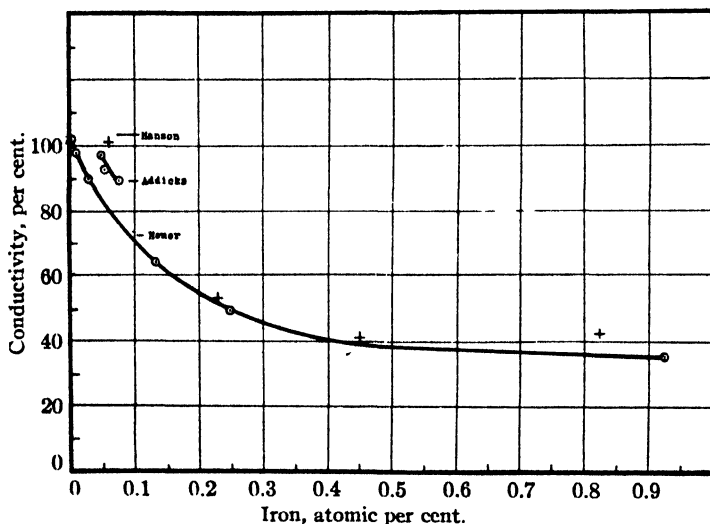


Fig. 4.—Effect of iron on conductivity of copper.

iron. The form of the curve is in accord with the general behavior of solid solutions as expressed by Guertler.² For comparison the data of

TABLE I
DATA FOR COPPER-IRON SYSTEM

Melt no.	Copper, wt. %	Oxygen, wt. %	Sulfur, wt. %	Iron, wt. %	Iron, atomic %	Conductivity %
22	100.000	0.0002	0.0001	0.0002	0.0002	102.10
4	99.995	.0007	.0006	.0071	.0080	97.60
3	99.975	.0007	.0006	.0241	.0274	90.05
20	99.880	.0002	.0003	.1212	.1379	64.80
18	99.778	.0001	.0001	.2179	.2481	49.6
21	99.159	.0003	.0004	.814	.925	35.6

Addicks and Hanson are plotted. The displacement of their values at low iron concentration confirms the original premise of this paper that ferrous oxide is present in their alloys.

The effect of small additions of iron upon the conductivity is shown to be considerable. For the first 0.0071% of iron present, the conductivity is lowered 4.5%, a rate of 634% for 1% iron. This great depression tends toward agreement with Norbury's⁹ generalization that solute elements far removed in the periodic system from the solvent metal cause the greater lowering in conductivity. Comparison, however, with Norbury's data for nickel solid solutions shows at once the more rapid lowering caused by iron. Norbury's idea seems to neglect the effect of the small solid solubility of iron.

The conductivity data confirm the expression of Hanson that the iron solid solubility at 750° is much less than the 3% originally reported by Ruer and Goerens.¹⁰

Hanson's suggestion that the solubility is less than 0.2% is not checked by the conductivity values. They seem to indicate between 0.3 and 0.4% as the limiting value.

Sample 22, the purest copper obtained in these experiments, had a conductivity of 102.1%. This can be compared with the values assembled by Wolff and Dellinger¹¹ for several samples of "pure" copper. Their highest value is 101.88%, obtained for electrolytic copper melted in a vacuum in an Acheson graphite crucible, drawn and tested as annealed wire. A piece of native Lake copper formed into wire without melting and tested in the annealed state yielded 101.87% conductivity. Their best value of several samples of electrolytic copper drawn to wire without melting and annealed is 101.60%. Meissner¹² observed 102.2% conductivity in a piece of electrolytically deposited wire which was carefully filed and ground to circular cross section and tested without drawing or annealing. This sample, however, cannot be regarded as statistically equivalent to the poly-crystalline aggregate obtained in wires which have been drawn and annealed. The electrolytic crystals may exhibit some preferred orientation and tend thereby to increase the conductivity toward the higher value of the copper single crystal.

The data for the binary system copper-cuprous oxide are assembled in Table II. The curve in Fig. 5 represents the relation of conductivity to volume per cent. of cuprous oxide calculated for a density of the oxide 6.0. Comparison is made to conductivity values calculated from the law of Le Chatelier, which requires that in systems whose components are

⁹ Norbury, *Trans. Faraday Soc.*, 16, 570 (1921); *J. Inst. Metals*, 33, 91 (1925).

¹⁰ Ruer and Goerens, *Ferrum*, 14, 49 (1917).

¹¹ Wolff and Dellinger, U. S. Bureau of Standards, *Sci. Paper*, 148, 1910.

¹² Meissner, *Ann. Physik*, 47, 1001 (1915).

insoluble in each other, the conductivity should be a linear function of the volume relationship. The observed conductivity is slightly lower than the calculated value, due to the occurrence of the cuprous oxide in the

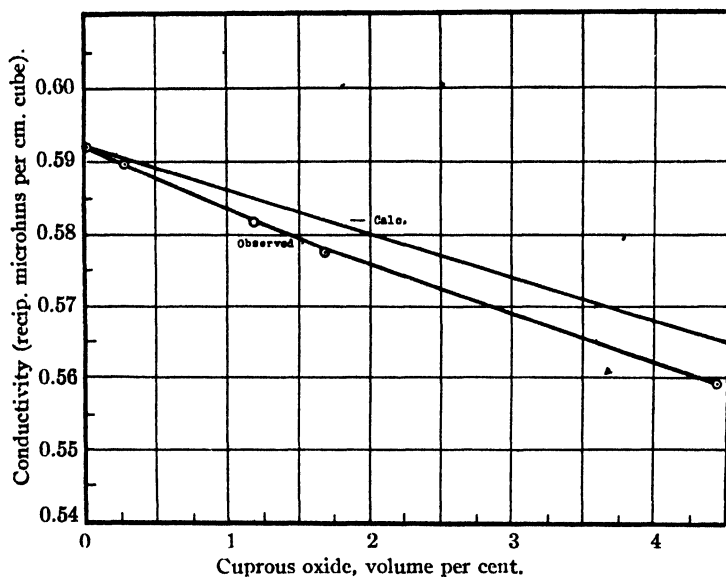


Fig. 5.—Effect of cuprous oxide on conductivity of copper.

test wires as elongated, spherical globules. If the oxide were present as cylinders, extending in uniform cross section throughout the length of the wire sample, the calculated and observed values should coincide.

TABLE II
DATA FOR BINARY SYSTEM COPPER-CUPROUS OXIDE

No.	Copper, wt. %	Oxygen, wt. %	Sulfur, wt. %	Iron, wt. %	Cuprous oxide	
					Wt. % calcd.	Vol. % calcd.
22	100.00	0.0002	0.0001	0.0002	0.0018	0.003
7	99.980	.0201	.0002	.0003	.180	.267
6	99.912	.0889	.0004	.0003	.800	1.181
5	99.876	.1266	.0002	.0002	1.133	1.670
9	99.664	.3373	.0002	.0002	3.019	4.411

No.	Cond., %	Resistivity, ohms/meter-g.	Density calcd.	Cond. obs. recip. microhms per cm. cube	Cond. calcd. recip. microhms per cm. cube	Cond. obs. minus calcd. recip. microhms per cm. cube
22	102.1	0.15013	8.89	0.5921	0.5921	0.0000
7	101.8	.15057	8.881	.5898	.5905	— .0007
6	100.8	.15207	8.852	.5821	.5855	— .0034
5	100.25	.15292	8.834	.5777	.5822	— .0045
9	97.9	.15657	8.757	.5593	.5660	— .0067

In Fig. 6, the conductivity is plotted against weight per cent. of oxygen. Data of Hanson,¹³ Antisell¹⁴ and Addicks³ are plotted for comparison. Antisell's figures seem to be the only ones capable of being reduced to a smooth curve. The curve indicated parallels closely the curve presented here, averaging perhaps 1.1% lower in conductivity. The lower conductivity is probably due to impurities other than oxygen in Antisell's metal.

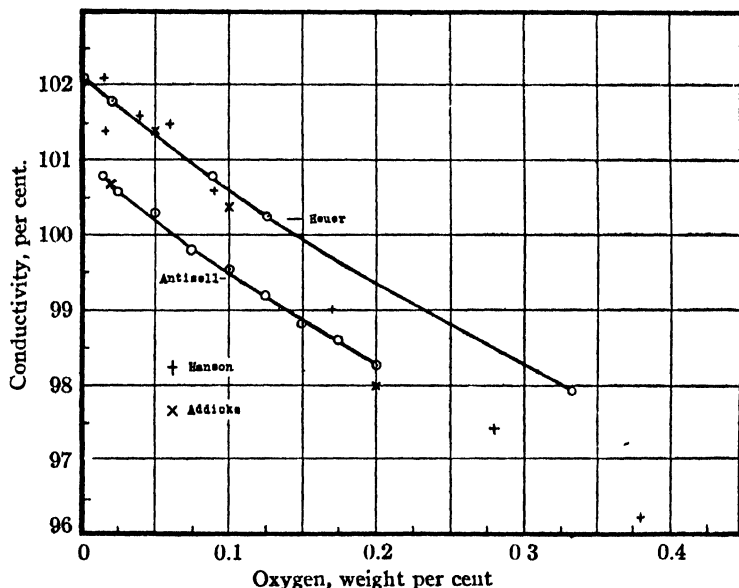


Fig. 6.—Effect of oxygen on conductivity of copper.

The data for the ternary melts are presented in Table III. The product mole fraction of iron \times mole fraction of cuprous oxide of these melts evaluates the position of the equilibrium in the fused alloy, assuming that while cooling no further separation of ferrous oxide from the metal phase takes place. The line abc is sufficiently defined by the order of magnitude of this product. In the melts Nos. 14, 16 and 17, the close agreement is perhaps, fortuitous, as no such analytical accuracy is claimed.

TABLE III
DATA FOR TERNARY MELTS

No.	Iron charged, %	Oxygen charged, %	Iron found, %	Oxygen found, %	Sulfur, %	Copper, %
14	0.13	0.02	0.0133	0.0035	0.0003	99.982
16	.11	.02	.0115	.0040	.0002	99.984
17	.05	.02	.0061	.0083	.0003	99.989
13	.10	.04	.0058	.0273	.0003	99.966

¹³ Hanson, *J. Inst. Metals*, 30, 197 (1923).

¹⁴ Antisell, *Trans. Am. Inst. Mining Met. Eng.*, 64, 432 (1921).

TABLE III (Concluded)

No.	Mole fraction Fe \times mole fraction Cu_2O	Cond. obs., %	Cond. calcd. from oxygen content (negl. Fe), %	Cond. lowering due to iron, %	Equiv. iron in solid sol., %	Micro- structure as cast
14	2.10×10^{-3}	101.80	102.05	0.25	0.0004	No eutectic
16	2.08×10^{-3}	101.85	102.05	.20	.0003	No eutectic
17	2.29×10^{-3}	102.0	102.0	.0	None	Copper plus eutectic
13	7.16×10^{-3}	101.85	101.7	— .15	None	Copper plus eutectic

The micro-structure of the alloys and the conductivity indicate the progress of the iron-copper oxide reaction at the eutectic temperature. Melts Nos. 14 and 16 contain copper, iron oxide and iron in solid solution of less than 0.0005%. No copper oxide eutectic remains. Melts Nos. 17 and 13 show residual copper oxide as eutectic. They contain iron in solid solution of the order of 0.0001%. These alloys indicate that the line TU is located on the diagram at such a low iron concentration as to practically coincide with the binary line of copper-oxygen. All alloys in the ternary system should react, therefore, at the eutectic temperature to form ferrous oxide. If the time be sufficient, the reaction will run either to complete oxidation of the iron or to the extinction of the cuprous oxide phase. Commercial copper containing the oxide eutectic should carry no iron in solid solution. The conductivity should be unaffected by the iron present.

The writer desires to express his appreciation of Dr. H. S. Lukens' kind interest in this work. To the U. S. Metals Refining Company and Mr. Sidney Rolle he is indebted for the conductivity measurements.

Summary

1. Thermodynamic calculations are advanced in this paper to question the validity of the existing data on the electrical conductivity of dilute solid solutions of iron in copper.

2. Revision of these data is made and iron is shown to reduce the conductivity of copper at the rate of 630% of the standard value for 1% iron.

3. The formation of ferrous oxide in alloys of copper, iron and oxygen is studied quantitatively. It is shown that iron can be completely oxidized in alloys containing cuprous oxide eutectic.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY, THE UNIVERSITY OF LIVERPOOL.]

THE THERMAL DECOMPOSITION OF OZONE. THE COMPUTATION OF VELOCITY CONSTANTS DETERMINED BY THE MANOMETRIC METHOD

By R. O. GRIFFITH AND A. MCKEOWN

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In a recent paper¹ on the thermal decomposition of ozone, Wulf and Tolman criticize our work² on the same subject. As part of their criticism appears to rest on a misunderstanding of the nature of the corrections which should be applied in such work, and as also the necessity for and magnitude of such corrections are not generally appreciated, we may be allowed to reply to their criticism and give a somewhat fuller account of our methods, together with their application to the experimental data of other investigators of this reaction.

In the first place, Wulf and Tolman take exception to the fact that the apparatus used by us to follow the decomposition at 100° contained "dead space"—the connecting lines from the reaction tube and the compensator tube to the manometer—which necessitated corrections to our pressure readings. This criticism might be pertinent if the "dead space" in question were large or the corrections improperly applied. Actually, however, the "dead space" in our apparatus was made reasonably small, the two tubes being joined directly through capillary taps to the sulfuric acid manometer, which was constructed of capillary tubing of 2 mm. internal bore. With the acid menisci level in the manometer, the volume unjacketed on either side was between 1.0 and 1.5 cc. in all our experiments. Finer capillary tubing for the manometer was avoided to obviate the risk of lag in the response of the manometer liquid to changes of pressure. As regards the condition that the reaction should take place at constant volume, this was sufficiently ensured, since a registered change of pressure of 200 mm. of sulfuric acid produced a change of volume of less than 0.4 cc. in a total of 150 cc. Indeed, the error involved in our measurements in this particular is considerably less than for the corresponding static experiments of Warburg³ and of Jahn,⁴ which, however, Wulf and Tolman view in a much less critical light. Thus with Jahn's apparatus, a change of pressure of 200 mm. of sulfuric acid would produce a change of volume of 0.078 cc. in a total of 6.3 cc.

Of much more importance, numerically, are the corrections to the registered pressure differences which the use of a moving manometric liquid

¹ Wulf and Tolman, *THIS JOURNAL*, **49**, 1183 (1927).

² Griffith and McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

³ Warburg, *Ann. Physik*, **9**, 1286 (1902).

⁴ Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

and the consequent variations in volumes of the "dead spaces" entail, and we have been at considerable pains to gage and apply these properly. Wulf and Tolman appear to associate the necessity for such corrections with poor technique; actually, however, similar but much greater corrections are necessary and were applied (though inadequately) in the work of Warburg and of Jahn. We proceed to indicate the nature and magnitude of these corrections.

The experimental arrangement commonly used consists essentially of a reaction and a compensator tube, capable of being jacketed at the same temperature, and connected to each other through a sulfuric acid manometer of capillary bore. We denote by V' and V'' the jacketed volumes of the reaction and compensator tubes, respectively, and by v the volume of unjacketed "dead space" on either side when the manometric levels are the same. If now with the whole apparatus at room temperature (Θ_1° , absolute) the manometer levels are identical, they will only be the same when the jackets are raised to the higher temperature Θ_2° , provided that $V' = V''$. Let us suppose that the tubes are filled at room temperature and to the same pressure (P_1 mm. of sulfuric acid), the one tube with the reaction mixture, the compensator with air or with oxygen. If a pressure difference of p_1 mm. of sulfuric acid, measured with the apparatus at room temperature, is subsequently developed due to reaction, the "true" increase of pressure which would have been developed, if measured, say, with a Bourdon Gauge, is not p_1 but $p_1\alpha_1$, where $\alpha_1 = 1 + \frac{P_1\gamma}{2} \left(\frac{1}{V'} + \frac{1}{V''} \right)$. Here γ is the volume in cc. per mm. of manometer tubing. However, an observed pressure difference of p_2 measured with the tubes at Θ_2° does not similarly correspond to a "true" increase of pressure of $p_2\alpha_2$, where $\alpha_2 = 1 + \frac{P_2\gamma}{2} \left(\frac{1}{V'} + \frac{1}{V''} \right)$, and P_2 is the total pressure (in mm. of sulfuric acid) in either tube at Θ_2° . That this is not so is due to the presence of "dead space" which is always at the lower temperature, Θ_1° . Neither is it true for the same reason that $(p_2\alpha_2/p_1\alpha_1)$ is equal to the ratio of absolute temperatures Θ_2/Θ_1 . The only correct way of interpreting an observed pressure difference p_2 (measured with the tubes at Θ_2°) is to find the value of p_1 or of $p_1\alpha_1$, to which it corresponds at room temperature. This may be effected either by calculation from the equation

$$p_2 = \frac{\Theta_2 (P_1 + \alpha_1 p_1) (V' + v)}{V' \Theta_1 + \left(v + \frac{p_2 \gamma}{2} \right) \Theta_2} - \frac{\Theta_2 P_1 (V'' + v)}{V'' \Theta_1 + \left(v - \frac{p_2 \gamma}{2} \right) \Theta_2} \quad (1)$$

or the ratio p_2/p_1 may be determined experimentally. In our work, we employed the latter method, and values of the ratio p_2/p_1 under different experimental conditions are denoted by R in our tables.⁵

⁵ Ref. 2, pp. 2089-2091.

For our apparatus we found experimentally and have confirmed by independent calculation from (1) that the ratio p_2/p_1 under a given set of conditions is practically independent of the value of the registered pressure difference p_2 . This implies that all corrections to our observed pressure readings affect only the absolute value of the derived velocity constants. The necessity for and use of corrections cannot be held responsible in our experiments for any observed "trend" in the value of a velocity constant throughout a single run. We may also remark that the conditions with regard to "dead space" in our apparatus were comparatively good (that is, $V' \approx V''$, and v and γ reasonably small compared with V'). In accordance with this we find that, had we employed the faulty method of correction used by Warburg and by Jahn (see next paragraph), the absolute values of our velocity constants would not have been affected by more than 4%.

Turning now to the work of Warburg and of Jahn, we must first note that their method of correcting their velocity constants to absolute units is equivalent to assuming that each observed pressure difference at Θ_2° corresponds to a true pressure difference of $p_2\alpha_2$ at the same temperature. This assumption is untrue; the more so as the "dead space" conditions in their experiments are considerably less favorable than in ours. We have attempted to estimate the errors thereby involved in their velocity constants in what follows.

The method of experimentation adopted by the two workers was the same, but slightly different from our own procedure. Their reaction and compensator tubes were first filled with oxygen to a known common pressure at room temperature Θ_1° . The oxygen in the reaction tube was then partially ozonized, the jacketing tubes raised to Θ_2° and the course of the reaction followed manometrically. Transforming again observed pressure differences p_2 at Θ_2° to the corresponding pressure differences p_1 which would be registered with the whole apparatus at Θ_1° , and hence to "true" pressure differences $p_1\alpha_1$ at Θ_1° , the relation now applying is

$$\alpha = \frac{\Theta_2 P_1 (V' + v)}{V' \Theta_1 + \left(v + \frac{p_2 \gamma}{2}\right) \Theta_2} = \frac{\Theta_2 (P_1 - p_1 \alpha_1) (V' + v)}{V' \Theta_1 + \left(v - \frac{p_2 \gamma}{2}\right) \Theta_2} \quad (2)$$

In applying this equation to the data of Jahn and of Warburg, it is necessary to make some assumption regarding their values of v (the "dead space" on either side of the manometer). For both sets of measurements we have made the reasonable estimate that this volume corresponds to the volume of 25 cm. of the capillary tubing employed. This makes $v = 0.195$ cc. in Jahn's apparatus; $v = 0.135$ cc. in Apparatus VII of Warburg; and $v = 0.202$ cc. in Warburg's Apparatus III.

The correct velocity constant k_a expressed in the units (liters/moles-minutes) is then obtained by transforming all the observed pressure differ-

ences p_2 in a given experiment into the corresponding values of $p_1\alpha_1$, using $p_1\alpha_1 = 0$ as the infinity reading,⁶ and substituting in the kinetic equation

$$k_a = 380 \times \frac{13.59}{1.84} \times 0.08207 \times \Theta_1 \times \frac{1}{(p_1\alpha_1)^2} \cdot \frac{d(p_1\alpha_1)}{dt} \quad (3)$$

TABLE I
EXPERIMENTS OF JAHN

Experiment A ₁				
$P_1 = 722 \times (13.59/1.84)$ mm. of sulfuric acid				
t	p_2	$p_1\alpha_1$	k_a	k_a (Jahn)
1	124	247.4	62.2	93.3
2	98	201.5	84.7	136
3	75	160.9	46.0	79.3
4	66	144.9	57.3	104
5	57	129.1	55.3	107
6	50	116.7	55.8	120
8.3	38	95.5		
∞	-14.7*	0		
		Mean	60.2	106 (108)
Experiment B ₁				
$P_1 = 539.1 \times (13.59/1.84)$ mm. of sulfuric acid				
t	p_2	$p_1\alpha_1$	k_a	k_a (Jahn)
2	90	157.4	90.8	139
3	72	129.9	85.9	139
4	60	111.5	75.6	128
5	52	99.1	76.3	144
7	40	80.9	68.2	139
8	36	74.8	63.4	139
10	30	65.6	52.6	129
12	26	59.5		
∞	-12*	0		
		Mean (?)	73	137 (140)

* This follows from the fact that at room temperature and *before osomising* the oxygen in the reaction tube, the two tubes are at the same pressure.

TABLE I (Concluded)

Experiment C _I				
$P_1 = 265.2 \times (13.59/1.84)$ mm. of sulfuric acid				
i	p_1	$p_1\alpha_1$	k_a	k_a (Jahn)
1	54	70.8	179	275
2	44	59.6	143	235
3	38	52.9	151	260
4	33	47.3	147	266
6	26	39.5		
∞	-9*	0		
		Mean 155	259	(258)

Considering first the data of Warburg for ozone decomposition, the "dead space" conditions are here not specially unfavorable, and recalculation of his results obtained with Tubes III and VII at 100°C. shows that his constants⁷ are in each case about 10% too high. At the higher temperature, 127°, the correction is greater; his constants should be about 15% greater than those given. It is when applied to Jahn's data, however, that the corrections assume very large proportions. In order to demonstrate this, we have recalculated the constants in three of Jahn's experiments (A_I, B_I, C_I, pp. 289 and 290 of his paper). The results are shown in Table I.

In the preceding table, the first column gives the time in minutes, the second the observed pressure differences in mm. sulfuric acid, and the third the corrected pressure differences, $p_1\alpha_1$, which are calculated from the figures in Col. 2 by use of Equation 2. The fourth column gives the values of the corrected velocity constants in absolute units calculated from Equation 3, and the last column the velocity constants which would be obtained by calculation according to the methods employed by Jahn. In both cases the constants are computed over successive time intervals. The bracketed figures at the foot of each final column are the values of k_a obtained by Jahn by the method of least squares. Before comparing the corrected velocity constants with those of Jahn, it is first to be observed that Jahn's calculations are faulty, owing to the use of incorrect estimates of the final pressures. His reaction and compensator tubes were at the same pressure at room temperature before ozonizing the contents of the former, and since the volume of the reaction tube is considerably greater than that of the compensator, the presence of "dead

⁷ The values of all the velocity constants in absolute units given in Warburg's paper are ten times too small. The 10% correction mentioned above refers to (Warburg's constants $\times 10$).

space" clearly necessitates that the final pressure difference at 127° will *not* be zero, as assumed by Jahn, but will be of opposite sign to the pressure effect caused by ozonization. This is shown in the tables by the asterisked values of the infinity readings for p_2 , which we have calculated by use of Equation 2. Errors in the value of p_∞ naturally affect the constancy of the calculated values of the velocity constants, and though this is partially disguised in Experiments A_I and C_I, it is fully revealed in Experiment B_I. Here the figures given in the final column, calculated with Jahn's assumption that p_2 at $t = \infty$ is zero, would appear to demonstrate an excellent bimolecular constant, but the figures in Col. 4 show that this agreement is fallacious and that proper correction gives a rapidly falling constant. In the other two experiments, the reaction was not followed for so long a time as in experiment B_I, and also there is a tendency for Jahn's constants to rise with time, both of which obscure the effect of correcting the infinity reading.

Comparing now Jahn's constants with the corrected ones, it is seen that his values in all three cases are of the order of 70–80% too high. It is not, however, our wish to lay any particular emphasis on the quantitative aspect of these figures, though we believe that they approximate to the true corrections necessary in his experiments; we desire simply to show that the published data of Jahn must be subject to quite large errors which are sufficient at least to render doubtful any conclusions drawn from his experiments by the manometric method. We draw attention to this, because Wulf and Tolman consider Jahn's experiments to demonstrate that "for ozonized oxygen which decomposes in accordance with the second order, the specific rate is closely inversely proportional to the total pressure." In our view, the uncertainties attached to Jahn's experimental data make any such conclusion of problematic worth.

We may summarize and compare the corrections necessary for "dead space" and moving manometric liquid in the experiments of Jahn, of Warburg and of ourselves in the following way. In our experiments the corrections necessary amount to and affect the observed velocity constants by between 7 and 22% depending on the total pressure; these corrections were properly applied. In Warburg's work the true corrections (for his experiments at 100°) amount to about 100%; the correction applied by him was somewhat less than this and leads to constants about 10% higher than those which should have been obtained. Finally, in Jahn's experiments the true correction lies between 200 and 95%, depending on the total pressure; the corrections actually applied by him were much too small, so that his constants are about 75% too high.

With regard to Wulf and Tolman's own experiments using the manometric method, they have applied no corrections to their pressure readings and in their paper they give no details of the dimensions of their mano-

meter capillary. However, from a later (private) communication of Dr. Wulf, it appears that in the majority of their static experiments manometer tubing of diameter 0.87 mm. was employed. The volume of their compensator being 322 cc., the error due to non-application of the appropriate pressure corrections only amounts to about 2%.

These authors have also objected to our method of determining the final pressure increase corresponding to complete de-ozonization in each run. Admittedly small errors might enter here, but in all experiments pressure readings were taken up to between three-quarters and seven-eighths of total decomposition of the ozone initially present. Granting as a liberal estimate a 5% error in our determination of the pressure increase, which would be caused by decomposition of the residual ozone, the maximum error in our value of p_{∞} is still less than 1%. Wulf and Tolman's own method of finding p_{∞} is open to more serious criticism. After following the reaction for some time at 100°, they raise the temperature of the reaction vessel to 150° for fifteen minutes and assume that de-ozonization is then complete. Actually, for the Runs 10 and 15 which they give in detail in Table I (pp. 1189-90 of their paper), this is far from being the case. Taking their own value of the bimolecular velocity coefficient for ozone decomposition at 147.7°, namely, $k_2 = 1.3 \times 10^4$ cc./moles-sec., and noting that in Run 10 the extent of decomposition at this temperature corresponds to a pressure increase of 2.77 cm. of sulfuric acid, it is easy to calculate that there still remains, at the end of the fifteen minutes at 150°, a concentration of ozone equivalent to 0.60 cm. in the same units. This means that each value of the pressure difference P given in their Table I (Run 10) is 0.60 cm. too low. The large errors thereby involved may be appreciated from the following table, in which a number of the values of k_2 for Run 10 as calculated by Wulf and Tolman (Col. 4) are compared with the values (Col. 5) recalculated by us from the corrected pressure differences.

It will be observed that the corrected velocity coefficients are 12 to 22% less than those given by Wulf and Tolman, and also that the fall in the value of k_2 (corr.) with time is more pronounced. The true extent of this trend in the velocity coefficient is more correctly obtained by calculating the velocity coefficients for successive time intervals by the relation

$$k'_2 = \frac{\text{const.}}{k_2 - k_1} \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

instead of referring each coefficient back to the conditions at $t = 0$ as is done in using the formula

$$k_2 = \frac{\text{const.}}{t} \left(\frac{1}{P} - \frac{1}{P_0} \right)$$

The value of k'_2 falls by about 33% while the concentration of ozone drops to one-third of its initial value.

TABLE II

t	P	P (corr.)	$k_2 \times 10^{-3}$ (W. and T.)	$k_2 \times 10^{-3}$ (corr.)	$k'_2 \times 10^{-3}$
0	9.61	10.21	1.82
12	8.24	8.84	2.07	1.82	1.68
15	7.98	8.58	2.03	1.79	1.65
19	7.65	8.25	2.01	1.76	1.61
25	7.22	7.82	1.98	1.73	1.62
31	6.82	7.42	1.97	1.71	1.49
37	6.49	7.09	1.94	1.68	1.57
46	6.03	6.63	1.93	1.65	1.51
58	5.52	6.12	1.91	1.62	1.43
72	5.04	5.64	1.88	1.59	1.44
87	4.60	5.20	1.87	1.56	1.46
102	4.22	4.82	1.87	1.54	1.41
117	3.90	4.50	1.87	1.53	1.36
132	3.63	4.23	1.87	1.51	1.27
160	3.23	3.83	1.85	1.47	1.22
202	2.77	3.37	1.83	1.42	

In a private communication Dr. Wulf points out that we have probably overestimated the extent of the errors in his infinity pressure readings since (1) we have taken no account of the times necessary for heating the reaction system up to 150° and for cooling after the superheating, and (2) the value we take for k_2 at the temperature of superheating may be too low. Instead of 1.3×10^4 , Dr. Wulf considers 1.9×10^4 to be a fairer estimate for k_2 at 150° , and he computes that 0.25 cm. is nearer the probable error in the final pressure of Run 10. Granted these possibilities, k'_2 in Experiment 10 would then fall from 1.96×10^3 to 1.5×10^3 throughout the run.

Summary

The application by various workers of the manometric method to the investigation of the thermal decomposition of ozone is discussed. It is shown that the derived velocity constants may be in error through (a)

incorrect interpretation of the observed pressure differences and (b) faulty estimation of the pressure readings corresponding to total decomposition. Warburg's data are slightly in error under (a), Wulf and Tolman's data rather more seriously in respect of (b), while Jahn's results are subject to very considerable errors under both heads.

LIVERPOOL, ENGLAND

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE DENSITIES OF COEXISTING LIQUID AND GASEOUS CARBON DIOXIDE AND THE SOLUBILITY OF WATER IN LIQUID CARBON DIOXIDE

H. H. LOWRY AND W. R. ERICKSON

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At the usually prevailing temperatures liquid carbon dioxide is less dense than water and not miscible with it. Therefore, theoretically, the degree of dryness of liquid carbon dioxide which has been separated mechanically from liquid water depends only on the solubility of the water in the liquid carbon dioxide. Experiments have been performed in an attempt to determine this solubility.

The method chosen was to determine the density of gaseous carbon dioxide in the coexisting state, both in the presence and absence of water. If water is appreciably soluble in liquid carbon dioxide, it should lower the vapor pressure and hence the density of the coexisting gaseous carbon dioxide. It may be calculated by means of Raoult's law that a solubility of 0.1%¹ by weight of water in liquid carbon dioxide will cause a decrease in vapor pressure of about 0.25%. The averages of three sets of determinations of the density of saturated gaseous carbon dioxide at temperatures ranging from -5.8 to 22.9° in the absence of water were 0.08% lower than the averages of two sets of determinations made in the presence of liquid water. This difference is opposite in sign to what would be expected if there were any solubility and is attributed entirely to experimental error.² The results obtained may be interpreted to indicate that the solubility of water in liquid carbon dioxide is less than 0.05% by weight over the temperature range investigated.

Experimental Method and Data

For the present investigation there was chosen the sealed tube method

¹ This is an upper limit of the solubility as suggested by experiments performed by Thomas Simon, *Z. ges. Kohlensäure Ind.*, 6, 239 (1900), and similar preliminary experiments performed by the authors.

² The average deviation of the experimentally determined gas density from the value calculated from the equation best fitting the entire data is 0.7%. Thus, while the probable error of any single datum is about 0.6%, consideration of the entire data indicates that the calculated values are probably correct within $\pm 0.1\%$.

of Young³ which has not previously been used for carbon dioxide. In this method different weights of carbon dioxide are sealed into glass tubes of sufficient strength to withstand the pressures developed, and the volumes occupied by the gas and liquid determined. This determination requires only the measurement of the length occupied by either gas or liquid in a tube which has been previously calibrated for volume.

Now,

$$W = v_l d_l + v_g d_g \quad (1)$$

where W is the total weight of carbon dioxide, v_l , v_g , d_l and d_g are the volumes and densities of liquid and gaseous carbon dioxide, respectively. W may be obtained at the end of an experiment by determining the difference in weight of the tube full and empty. Since in Equation 1 there are two unknowns, d_l and d_g , it is necessary to make determinations on two tubes either of different total volumes or containing different total weights of carbon dioxide.

The experimental error of the method is largely one of reading length. As used by Young on many organic liquids, where lengths were read only to 0.1 mm., the errors under different conditions ranged from 0.5 to 6%.⁴ Nevertheless his data⁵ are apparently consistent to about 0.1%. In the present investigation lengths were read with a traveling microscope to 0.002 mm. Temperature was determined with a thermometer calibrated at the ice-point, 0°, and at the transition temperature of sodium sulfate decahydrate, 32.8°. On account of the great difference in density of the gas and liquid phases, correction was also made for the volume of the liquid meniscus,⁶ which otherwise would be included with the gas volume. Corrections based on direct measurements were also applied to the volume of the tube for distortion introduced on sealing the ends of the tube. The reading of the length of tube filled by gas and liquid was in each case determined after the temperature was raised and again after it was lowered to the temperature of the experiment. The lengths so obtained agreed on the average to 0.020 mm. The arithmetical average of the two readings was used in the calculations. In order to facilitate reaching thermal equilibrium a small rod of permalloy was sealed in the tube for stirring the liquid. This stirring was accomplished by raising and lowering a small electromagnet around the tube. Calculations showed that the volume increase in the tube due to expansion caused by the maximum pressure developed within it would amount to only 0.02% of the total volume and hence no correction was made. Calculation also showed that changes in volume of the tube due to temperature changes are of the same order of magnitude and could also be neglected. Even with these corrections and precautions, analysis of the data obtained in three separate runs indicates that the average deviation of a single observation for the liquid density is $\pm 0.1\%$, and since an error in determination of the liquid density introduces a larger error, opposite in sign, in the determination of the gas density, the average deviation of a single observation of gas density is greater, that is, 0.7%. Hence, to obtain a much higher

³ Young, *Trans. Chem. Soc.*, **59**, 37 (1891).

⁴ Ref. 3, p. 126.

⁵ As summarized in *Proc. Roy. Soc. Dublin*, **12**, 374 (1910). It is not clear whether these data are original observations or interpolated values.

⁶ "International Critical Tables," Vol. 1, pp. 72 and 73, 1926. For this purpose values of the surface tension of liquid carbon dioxide were obtained from the data given in the Landolt-Börnstein Tabellen, 5th edition, 1923.

degree of accuracy, a larger number of observations would be necessary at each temperature. It may be estimated, however, that mathematical analysis of the data of this investigation permits values of coëxisting liquid and gaseous carbon dioxide to be calculated with an accuracy of $\pm 0.1\%$ over the temperature range -5.8 to 22.9° .

The data obtained are given in Table I. For purposes of comparison there are included in this table values of d_l , d_g and $(d_l + d_g)/2$ calculated from the equations

$$d_l = 0.4683 + 0.001442(t_k - t) + 0.1318 \sqrt[3]{(t_k - t)} \quad (2)^7$$

$$d_g = 0.4683 + 0.001442(t_k - t) - 0.1318 \sqrt[3]{(t_k - t)} \quad (3)$$

and

$$(d_l + d_g)/2 = 0.4683 + 0.001442(t_k - t) \quad (4)$$

TABLE I
THE DENSITIES OF COEXISTING LIQUID AND GASEOUS CARBON DIOXIDE

$t, ^\circ\text{C.}$	d_l			d_g			$(d_l + d_g)/2$		
	Obs.	Calcd.	Calcd.-obs.	Obs.	Calcd.	Calcd.-obs.	Obs.	Calcd.	Calcd.-obs.
22.9	0.7422	0.7448	+0.0026	0.2163	0.2152	-0.0011	0.4793	0.4800	+0.0007
17.2	.8045	.8044	- .0001	.1721	.1720	- .0001	.4883	.4882	- .0001
15.2	.8216	.8216	.0000	.1607	.1606	- .0001	.4912	.4911	- .0001
11.2	.8547	.8535	- .0012	.1390	.1401	+ .0011	.4969	.4968	- .0001
6.2	.8878	.8886	+ .0008	.1217	.1196	- .0021	.5048	.5041	- .0007
1.2	.9198	.9201	+ .0003	.1029	.1025	- .0004	.5114	.5113	- .0001
-1.8	.9378	.9376	- .0002	.0940	.0936	- .0004	.5159	.5156	- .0003
-5.8	.9604	.9598	- .0006	.0803	.0828	+ .0025	.5204	.5213	+ .0009

For these calculations, t_k was assumed to be 31.0° ⁸ and the critical density, 0.4683, was obtained by plotting $(d_l + d_g)/2$ against t and extrapolating the straight line thus obtained to 31.0° . This method of obtaining the critical density, first suggested by Cailletet and Mathias,⁹ is very convenient, since by averaging the densities the errors are minimized, due to the fact that in the method used too high a value of the density of either phase is necessarily accompanied by too low a value of the other phase. Since the liquid density is just as much greater as the gas density is lower than their average, the equation giving either as a function of temperature should be obtained by addition to or subtraction from the equation representing their average of an additional term. The agreement of the data with Equations 2, 3 and 4 showed that the data may be satisfactorily represented in this way.

Since the values obtained in the presence of excess water agree with the

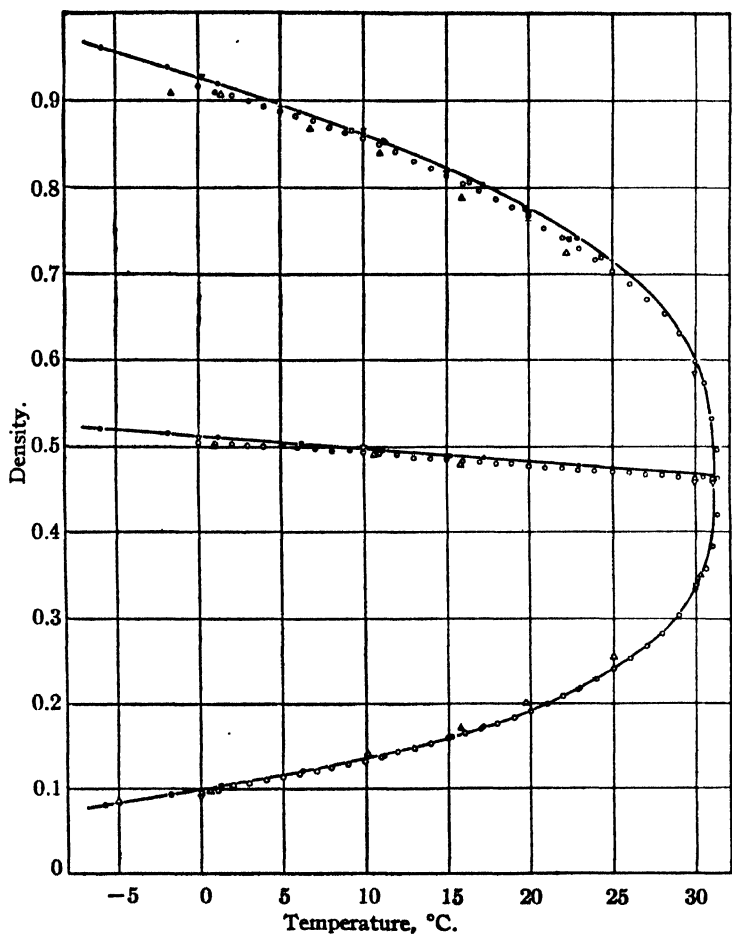
⁷ Attention might be called to the fact that for all materials for which the data are available the densities of the coëxisting gaseous and liquid phase are less or greater, respectively, than their average densities at any temperature, within about 100° of their critical temperature, by a quantity $a \sqrt[n]{t_k - t}$, where $n = 3.000$.

A theoretical discussion of this relationship is given by S. Sugden, *J. Chem. Soc.*, 1927, p. 1780 ($n = 10/3$).

⁸ Landolt-Börnstein Tabellen, 5th edition, 1923.

⁹ Cailletet and Mathias, *Compt. rend.*, 102, 1202 (1886).

values given in Table I within the experimental error, they will not be separately tabulated. It should be stated that at about 4° the water in the tube appeared to freeze and offered considerable resistance to passage of the stirrer. According to W. Hempel and J. Seidel¹⁰ carbon dioxide



Δ Cailletet and Mathias; \circ Amagat; \square Behn; $+$ Jenkin; \bullet Lowry and Erickson; ∇ Keyes and Kenny.

Fig. 1.—The densities of coexisting liquid and gaseous carbon dioxide.

forms a hydrate, $\text{CO}_2 \cdot 9\text{H}_2\text{O}$, which melts at 8° and 43 atmospheres. It seems probable that, due to supercooling, the hydrate did not form at the melting point in our experiments.

The data obtained in this investigation are plotted in Fig. 1. For

¹⁰ Hempel and Seidel, *Ber.*, 31, 2997 (1898). (See also P. Villard, *Compt. rend.*, 119, 368 (1894) who describes the hydrate as $\text{CO}_2 \cdot 6\text{H}_2\text{O}$.)

purposes of comparison with other recorded data there are also plotted the results of previous investigators. The curves are drawn to fit Equations 2, 3 and 4. In Table II there is presented a summary of the interpolated values at 5° intervals from -5° to the critical temperature for all observers except Andréeff,¹¹ whose points are undoubtedly in considerable error. The values of density given by F. G. Keyes and A. W. Kenny,¹² although not original data, are also included in the figure and in Table II.

TABLE II

INTERPOLATED VALUES OF THE DENSITIES OF COEXISTING LIQUID AND GASEOUS CARBON DIOXIDE AT TEMPERATURES FROM -5 TO 31°

<i>t</i> , °C.	Liquid						Gaseous			
	C&M	A	B	J	K&K	L&E	C&M	A	K&K	L&E
31.0	0.459 ^b	0.536 ^c	0.4597	0.4683	0.396 ^b	0.392 ^c	0.4597	0.4683
30.0	.556 ^b	.598	0.5985841	.6016	.355	.334	.3370	.3380
25.0	.685 ^b	.703	.711	0.717	.7015	.7165	.254	.240	.2391	.2375
20.0	.755	.766	.772	.761	.7698	.7784	.203	.190	.1883	.1910
15.0	.807	.814	.819	.819	.8228	.8236	.167	.158	.1518	.1594
10.0	.848	.856	.860	.861	.8636	.8626	.139	.133	.1323	.1350
5.0	.883	.888	.893	.894	.8980	.8966	.117	.114	.1090	.1154
0.0	.913	.914	.925	.925	.9268	.9273	.099	.096	.0958	.0993
-5.0	.9389549551	.9556	.0840825	.0854

^a C&M, Cailletet and Mathias;⁹ A, Amagat;¹⁰ B, Behn;¹⁴ J, Jenkin;¹⁵ K&K, Keyes and Kenny;¹² L&E, Lowry and Erickson.

^b Extrapolated according to formula given by Cailletet and Mathias.

^c According to Amagat's data, $t_k = 31.35$ and $d_k = d_g = 0.464$.

Consideration of the data given in Table II shows in general that there is quite satisfactory agreement among the observers. It is evident, however, that the equations used by Keyes and Kenny give values of density considerably too low for the liquid phase at the higher temperatures and for the gas phase at the lower temperatures.

Summary

The densities of coëxistent liquid and gaseous carbon dioxide have been measured and it has been shown that they can be satisfactorily represented by equations involving the first and one-third powers of the temperature on the critical scale over a temperature range from -5.8 to 22.9°. A comparison of the data of other observers with these data has shown them to be in substantial agreement. The data indicate that the critical density of carbon dioxide is 0.4683, which may be compared with the value 0.464 of Amagat and 0.4597, as judged by Keyes and Kenny, from analysis of earlier data.

¹¹ Andréeff, *Ann.*, 110, 1 (1859).

¹² Keyes and Kenny, *J. Am. Soc. Refrig. Eng.*, 3, 48 (1916).

¹³ Amagat, *Compt. rend.*, 114, 1093 (1892).

¹⁴ Behn, *Ann. Physik*, [4] 3, 733 (1900).

¹⁵ Jenkin, *Proc. Roy. Soc. (London)*, 98, 170 (1920).

It has been shown that the density of saturated carbon dioxide vapor is the same in the presence or absence of water within the experimental error. Assuming applicability of Raoult's law and direct proportionality between vapor pressure and vapor density, it may be calculated that the solubility of water in liquid carbon dioxide is less than about 0.05% by weight over the temperature range of this investigation. Attention has been called to qualitative evidence of the formation of a solid hydrate of carbon dioxide at about -1° .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TORONTO]

THE SYSTEM POTASSIUM CARBONATE, SODIUM CARBONATE AND WATER AT 40° AND THE TRIHYDRATE OF SODIUM CARBONATE

By J. W. BAIN

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An investigation of this system has been proceeding in this Laboratory for a number of years and brief statements of progress have appeared elsewhere.¹ The excellent investigations of Hill and Miller² have thrown a flood of light upon the various phases which exist between 20 and 40° and have explained some of the difficulties encountered in the work here; conflicting results which were met with early in our study have focused attention on the isotherm of 40° . This communication gives additional data which had escaped the notice of previous investigators.

At the outset of our work a number of determinations confirmed the accuracy of the results of Osaka³ and of Kremann and Zitek⁴ regarding the composition of the saturated solution; the residues were not analyzed and the existence of the double salt $K_2CO_3 \cdot Na_2CO_3 \cdot 12H_2O$ was assumed, instead of the solid solution $(K_2Na_2)CO_3 \cdot 6H_2O$ found by Hill and Miller. In order to be well beyond the transition point of the supposed double salt, the temperature of 40° was selected for the next isotherm. An inspection of the solubility curves for potassium and sodium carbonates showed that there was only a slight variation in solubility in both cases with a change of temperature of several degrees, and for this reason an ordinary thermometer divided to single degrees was considered sufficiently accurate to show the temperature of the bath; this choice gave much trouble subsequently.

¹ (a) Bain and Oliver, *Trans. Roy. Soc. Canada*, **10**, III, 65-66 (1910); (b) Bain, **18**, III, 273-274 (1924).

² Hill and Miller, *THIS JOURNAL*, **49**, 669 (1927).

³ Osaka, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **3**, 51 (1911).

⁴ Kremann and Zitek, *Monatsh.*, **30**, 323 (1909).

Experimental Methods

The carbonates used were of c. p. quality and each lot was analyzed before use; the samples conformed to the usual standards. Weighed quantities of the components were placed in L-shaped glass tubes which were rocked to and fro in the bath, the movement of a large bubble of air producing a stirring action. From time to time the tubes were removed and shaken vigorously to break up crusts, and in some instances the solid phase was filtered off, ground in a mortar and returned to the tube. The samples were withdrawn by a weighing pipet and, after dilution, the sodium and potassium were determined as chlorides in one portion, an operation in which wide glass tubes with bent-up, drawn-out ends⁶ were almost indispensable; in another portion potassium was determined as perchlorate. All determinations were made in duplicate and the agreement was excellent.

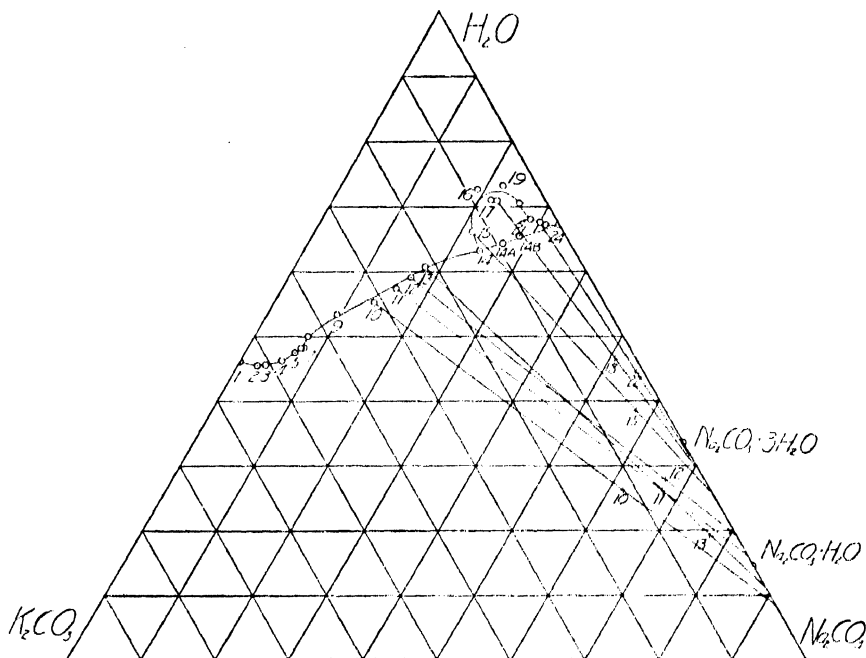


Fig. 1.

The solid phases were filtered off, sucked dry, dissolved and analyzed as above. Hill and Miller's method of centrifuging, which was only published toward the conclusion of our work, has been tried and is undoubtedly a great improvement. During the course of the investigation sixty-seven separate experiments have been carried out, the large number being due to the difficulty in securing solutions in equilibrium with a stable phase; from these the following results have been selected; temperature, 40°.

The curves lying to the left of Point 14 were thoroughly established by April, 1924, but no concordant results could be obtained in the remainder of the field. Variable results from solutions of the same composition led to the conclusion that equilibrium was only very slowly attained and,

⁵ Ostwald-Luther, "Physiko-chemischer Messungen," 4th edition, p. 309.

TABLE I
 RESULTS OF EXPERIMENTS

No.	Solution		Residue		Sp. gr., 40°/20°	Days shaken	Solid phase ^a
	K ₂ CO ₃	Na ₂ CO ₃	K ₂ CO ₃	Na ₂ CO ₃			
1	53.9	K ₂ /s
2	51.9	2.7	1.582	7	K ₂ /s
3	50.7	3.8	1.581	7	K ₂ /s + KN
4	48.1	5.6	1.586	5	KN
5	45.8	6.8	1.563	15	KN
6	44.7	7.2	1.557	89	KN + N ₁
7	44.2	7.2	1.567	6	KN + N ₁
8	42.8	7.2	1.550	6	N ₁
9	37.1	9.5	1.508	56	N ₁
10	31.1	13.6	11.8	62.0	1.496	58	N ₁
11	27.1	15.5	6.6	67.5	1.451	61	N ₁
12	24.3	16.7	5.0	67.2	1.424	94	N ₁
13	21.6	17.8	3.6	77.3	1.447	99	N ₁
14	12.9	24.0	1.387	91	N ₁ + N ₂
14A	9.1	26.6	1.374	15	N ₁
14B	6.2	28.5	1.366	47	N ₁
15	12.2	21.6	4.0	57.5	1.341	104	N ₂
16	8.4	19.0	1.441	107	N ₂
17	7.4	21.6	1.290	111	N ₂
18	6.6	22.5	2.6	50.7	1.291	113	N ₂
19	4.8	22.1	1.272	113	N ₂
20	3.7	25.8	1.292	115	N ₂
21	3.6	28.6	34	N ₂
22	2.3	30.0	0.8	54.6	1.328	120	N ₂
23	1.8	31.1	1.326	12	N ₂
24	..	32.8	N ₂

^a For convenience, the symbols of Hill and Miller have been used. K₂/s = K₂CO₃·3/2H₂O; KN = K₂CO₃·Na₂CO₃; N₁ = Na₂CO₃·H₂O; N₂ = Na₂CO₃·3H₂O. The solid phases in Nos. 3 to 7 were not determined and are assigned on the basis of Hill and Miller's isotherm at 36°.

consequently, the period of shaking was increased first to a fortnight and then to greater lengths as indicated in the table. The conclusion was finally reached that the temperature of the bath oscillated about the temperature of a transition point, and that a new hydrate of sodium carbonate was present. It is very easy to obtain solutions supersaturated with respect to the monohydrate and of the numerous results which were obtained in consequence, numbers 14A and 14B are placed on the diagram upon a dotted line indicating the metastable prolongation of the curve stretching from 7 to 14.

As is shown in the diagram, the projection of the tie lines between the points 14, 18 and 22, indicating the composition of the solution and of the moist residue, intersect the side of the triangle at very obtuse angles and consequently little reliance can be placed upon them. It was, therefore, necessary to investigate the composition of the solid phase in equi-

librium with solutions lying to the right of point 14 by some other method.

A sample of sodium carbonate which had been shaken with an amount of water sufficient only to partially dissolve it, was filtered in a tube with a Jena glass disk surrounded by water at 42°; after a few moments' suction the moist salt was washed with a very small quantity of ether, poured on dropwise, and was then rapidly removed to a stoppered weighing bottle.

Anal. 1.0702 g. titrated with 0.9562 *N* HCl, using methyl orange, required 14.0 cc., = 0.7102 g. Na_2CO_3 , whence $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 1:2.98$ 0.6768 g. heated at 270–300° gave 0.4507 g. Na_2CO_3 , whence $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 1:2.95$.

To confirm this result, 50.0 g. of Na_2CO_3 , 4.0 g. of NaCl and 60.18 g. of H_2O were shaken for a number of days at 41°; in the filtered solution there were found: 0.6771 g. of NaCl = 0.5015 g. of Na_2CO_3 + 0.1202 g. of NaCl in 1.9355 g. of solution, on the assumption that all the NaCl present was in solution; the NaCl alone = 0.1202 g.; H_2O as solution = 43.64 g.; Na_2CO_3 in solid phase, 33.20 g.; hence $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 1:2.93$.

Samples of the solid phase were also centrifuged as suggested by Hill and Miller and it was found after a number of trials that great care had to be taken to prevent the sample from falling below 40°, since otherwise the results were unsatisfactory.

Anal. 0.5479 g. of the centrifuged salt lost on heating 0.1850 g. of H_2O , whence $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 1:3.02$.

The results of these independent methods, taken together with the intersections of the tie lines on the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ side of the triangle, are evidence of the existence of a trihydrate of sodium carbonate, the solubility of which is represented by the curve from Points 14 to 24. Solutions prepared by agitating sodium carbonate for a few hours at 40° or over are saturated with respect to the metastable monohydrate but are supersaturated with respect to the stable trihydrate; since the change from one form to the other is slow, the investigators of the solubility of this salt, even such careful and experienced workers as Wells and McAdam,⁶ have overlooked the existence of the trihydrate. The present data on solubility above 40° are undoubtedly in error and will be further investigated in this Laboratory.

It is not yet possible to state definitely how long a sample must be shaken at 41° or slightly higher in order that the complete conversion to the trihydrate may be assured, but at present it is believed that not less than six days should be allowed.

An attempt was made to determine with some precision the transition point by the thermal method, using the procedure of Richards.⁷ A series of runs was made with slowly rising and falling temperatures which yielded

⁶ Wells and McAdam, *THIS JOURNAL*, 29, 721 (1907).

⁷ Richards, *Am. J. Sci.*, [4] 6, 201 (1898).

definite indications of a transition point although the constancy of temperature lasted only for a few minutes. The change of one hydrate into the other proceeds slowly, and the existence of the monohydrate above the transition point for days as a metastable form is indicative of this sluggishness; the trihydrate appears to pass over into the monohydrate more rapidly but the rate is still low. The transition of the trihydrate into the monohydrate is accompanied by the evolution of heat. When these difficulties had developed during the first few runs, attempts were made to obtain more favorable conditions, that is, the monohydrate prepared at 37° was added to the trihydrate at 41° and the mixture slowly cooled and then heated again. The converse procedure was also tried but no method of accelerating the change from one hydrate to the other could be found. In all, seventeen runs were made; the arrests with rising temperature occurred from 39.60 to 39.98° and on cooling at 39.97 to 39.85° . The transition temperature is, therefore, assumed for the present to be $39.8^{\circ} \pm 0.1^{\circ}$.

The compound $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ has not been previously described except as associated with the efflorescent soda in the dried river beds of the Cordilleras,⁸ and as a deposit from hot springs near Saxby River, Queensland.⁹

The greater portion of the experimental work in this investigation has been carried out by a number of students, whose assistance is gratefully acknowledged.

Summary

1. The system $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ has been studied at 40° .
2. The existence of the trihydrate of sodium carbonate has been proved.
3. The transition point in the system $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is $39.8 \pm 0.1^{\circ}$.
4. The solubility data for sodium carbonate at 40° and for some unknown higher range in temperature, as at present recorded, refer to the composition of solutions in equilibrium with the metastable monohydrate and require revision.

TORONTO, CANADA

⁸ Schickendantz, *Ann.*, **155**, 359 (1870)

⁹ Daintree, *Quart. J. Geol. Soc.*, **28**, 285 (1872).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 148]

THE POTENTIOMETRIC DETERMINATION OF INDIUM

By ULRIC B. BRAY¹ AND H. DARWIN KIRSCHMAN

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Introduction

An accurate and fairly rapid method of analysis of indium solutions has become desirable in order to facilitate further investigations on indium in this Laboratory. The two methods described in the literature are the electrodeposition^{2,3,4} of the metal and the weighing of the indium oxide obtained by igniting the precipitated hydroxide.^{5,6}

The electrodeposition of indium from a chloride solution, either in the presence of formic acid and ammonia or in the presence of Rochelle salt, as suggested by earlier authors, was found unsuitable for an accurate quantitative determination with chloride solutions. However, by using a sulfate solution, with a current density of 0.4 ampere per square decimeter and a potential of about 4 volts, very adherent deposits of indium with no platinum black were obtained with a rotating cathode. But the difficulty of precipitating the last few milligrams of indium from the solution, as observed by the present authors in over a dozen electroplating experiments, makes this an uncertain method of analysis. As mentioned by Dennis and Geer, the electrodeposition of indium was found to be an excellent method of purifying it from iron, since one deposition from a sulfuric acid solution of the crude oxide gave a metal which showed no test for iron with potassium thiocyanate.

Determinations as the oxide, In_2O_3 , were made by essentially the method of Thiel and Koelsch as follows. The hydroxide was precipitated from the solution of the chloride by the addition of a slight excess of freshly filtered ammonium hydroxide. The white, flocculent precipitate was washed by decantation until free from chlorides with a 1% solution of ammonium nitrate and filtered into a Gooch crucible. In the first set of determinations the crucibles were heated over a blast-lamp for thirty minutes, cooled and weighed. This was repeated but a constant weight was not obtained. In the second set of determinations the crucibles were placed in an electric furnace and brought to about 850° for thirty minutes. This was repeated until the weight was constant to 0.2 mg. The crucibles

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² Kollock and Smith, *THIS JOURNAL*, **32**, 1248 (1910).

³ Dennis and Geer, *ibid.*, **26**, 437 (1904).

⁴ Mathers, *ibid.*, **29**, 485 (1907).

⁵ (a) Thiel and Koelsch, *Z. anorg. Chem.*, **66**, 288 (1910). (b) *ibid.*, **40**, 280 (1904).

⁶ Dennis and Bridgman, *THIS JOURNAL*, **40**, 1531 (1918).

were then heated in the furnace at about 900° for about forty minutes, when a loss of weight of several milligrams occurred.

Both of these methods were thus found by the authors to be not well suited to the purpose at hand. A new method of analysis was therefore worked out. This consists in titrating the indium with potassium ferrocyanide and determining the end-point potentiometrically. Since indium forms with potassium ferrocyanide a precipitate which is insoluble in nitric and sulfuric acids and in hydrochloric acid up to 4 *N*, and since it does not give an insoluble compound with potassium ferricyanide, the system lends itself to this method of electrotitration. The composition of the insoluble compound formed during the titration has been investigated in order to obtain a convenient method of standardizing the ferrocyanide solution.

Apparatus

The apparatus used consists of (1) a motor-driven stirrer; (2) a 1 *N* KCl-calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of small (0.05 cm. diameter) platinum wire through the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup "Type K" potentiometer with a high sensitivity galvanometer. A beaker containing the unknown solution diluted to about 300 cc. is a convenient size. For the inert metal electrode a short platinum wire rather than a foil electrode is used. For the reference electrode a 1 *N* calomel half-cell is satisfactory and consequently no attempt has been made to use a system of bimetallic electrodes.^{7,8}

The Method of Titration

Preliminary experiments showed that solutions of indium chloride titrated potentiometrically give curves almost identical in form with those obtained by titrating zinc^{9,10,11,12} in acid solution at 70° with potassium ferrocyanide. During the potentiometric titration, equilibrium is reached at the oxidation-reduction electrode in less than thirty seconds, except in the immediate vicinity of the end-point where the voltage is changing rapidly. The ratio of indium solution to ferrocyanide solution obtained by taking the mid-point of the vertical section of the curve as the end-point was found to be quite constant. Stock solutions of carefully purified indium chloride were prepared by dissolving well-washed precipitates of the hydroxide in a slight excess of a constant-boiling solution of hydrochloric acid and diluting to about 0.03 or 0.07 molal.

The effects of acid, neutral salts, concentration of indium salt and temperature on the ratio of the two solutions were studied. In all experiments the ferrocyanide was added to the indium solution from the buret,

⁷ Willard and Fenwick, *THIS JOURNAL*, **44**, 2504 (1922).

⁸ Van Name and Fenwick, *ibid.*, **47**, 9 (1925).

⁹ Bichowsky, *J. Ind. Eng. Chem.*, **9**, 668 (1917).

¹⁰ Müller, *Z. anorg. Chem.*, **128**, 126 (1923).

¹¹ Treadwell and Chevert, *Helv. Chim. Acta*, **5**, 633 (1922); (b) **6**, 550, 559 (1923).

¹² Verzijl and Kolthoff, *Rec. trav. chim.*, **43**, 380 (1924).

no attempt being made to study the effect of adding the indium to the ferrocyanide, since satisfactory results were obtained by the easier method. Voltages were read to one millivolt as soon as equilibrium was substantially established after each addition. At the beginning of the titration and up to within two or three cubic centimeters of the end-point the ferrocyanide was allowed to run from the buret fairly rapidly, because the final curve was found to be independent of the rate of addition. The first part of the curve is of little or no importance and depends to a considerable extent on the previous treatment of the platinum wire electrode. The voltage gradually rises with the addition of the ferrocyanide solution to about 0.62 volt and then remains practically constant until within a few cubic centimeters of the end-point, after which a gradual decrease of potential occurs. Thereafter additions of 0.5 cc. are made, and finally of 0.1 cc. as the end-point is more closely approached. Curve A of Fig. 1 is typical of the behavior at room temperature.

The effect of acid more concentrated than 0.05 *N* in the final solution is both to decrease the drop in potential at the end-point and to make the decrease take place gradually instead of suddenly. The effect of neutral salt is

essentially the same as that of acid; thus, several titrations made with solutions to which both hydrochloric acid and potassium acetate had been added gave curves similar to those obtained by using dilute acid with a corresponding amount of potassium chloride. When the decrease in voltage takes place gradually, as in solutions of high ionic strength, it is very difficult to obtain an accurate end-point. The curves obtained in these cases were similar to Curve B in Fig. 1.

Titration were made at room temperature (about $25 \pm 2^\circ$), at 45° and at 85° . The best curves were obtained at room temperature. At 45° the curve is still fairly good but at 85° the drop in voltage is too gradual. The end-points were in general determined independently by the two

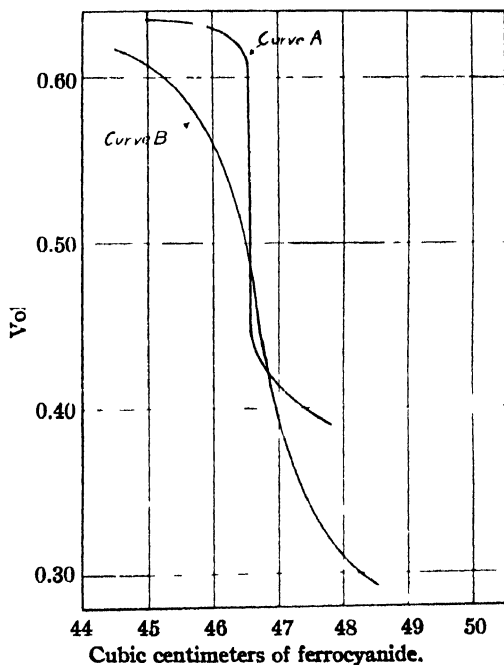


Fig. 1.

authors from the titration data and seldom differed by more than 0.02 cc. The standard ferrocyanide solutions were kept in black lacquered bottles under an atmosphere of nitrogen.

In Table I are given the results of a number of titrations of two stock solutions, A and B, of indium chloride with the ferrocyanide solution. They show the accuracy with which the end-point can be determined under different conditions. The indium chloride solution was always about 0.02 *N* in hydrochloric acid.

TABLE I

TITRATIONS OF INDIUM CHLORIDE SOLUTIONS WITH POTASSIUM FERROCYANIDE					
Stock sol.	InCl ₃ solution, g.	K ₄ Fe(CN) ₆ solution, cc.	Ratio	Temp., °C.	Volume of solution
A	20.06	20.38	1.016	Room	350
	20.07	20.38	1.016	Room	350
	40.69	41.30	1.015	Room	350
	20.00	20.24	1.012	Room	700
	20.14	20.48	1.017	45°	350
B	10.36	23.80	0.07321	Room	350
	15.80	36.32	.07326	Room	350

Composition of the Compound between Indium and Potassium Ferrocyanide

While the reproducibility of the ratios of indium solution to ferrocyanide solution shows the end-point to be sharp, it is desirable to know the ratio of indium to ferrocyanide in the precipitated compound, in order not to have to rely upon a pure indium preparation as the means of standardizing the ferrocyanide solution. To establish the composition of this compound, it was first necessary to determine the actual molality of the ferrocyanide in the solution used. This was done as follows. A solution of potassium ferrocyanide was made 0.05 normal as closely as possible by weighing out selected crystals of the trihydrate, adding 0.5 g. of potassium ferricyanide, dissolving in water and diluting to exactly one liter. This 0.05 formal solution was then titrated electrometrically against two very carefully standardized zinc solutions which one of the authors had prepared for electromotive force measurements on zinc sulfate.¹³ Assuming the molality of the potassium ferrocyanide to be 0.05 in correspondence with the weight of crystals taken, the ratio of zinc to ferrocyanide in the titration was found to be 1.505 and 1.508 for the two separate zinc solutions. This is in agreement with Treadwell and Chevert,¹⁴ who have

¹³ U. B. Bray, *THIS JOURNAL*, **49**, 2372 (1927). The method of standardizing these zinc solutions was the potentiometric method, using another ferrocyanide solution. The basis of the standardization was Kahlbaum's "zur Analyse" zinc sticks and anhydrous zinc sulfate. All titrations were made under similar conditions of concentration, temperature and acidity.

¹⁴ Ref. 11. Although Verzijl and Kolthoff (ref. 12) report an error of a few tenths of a per cent. from the theoretical potentiometric end-point in ferrocyanide precipita-

shown that the insoluble compound formed between potassium ferrocyanide and zinc is $\text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2$. The exact molality of ferrocyanide solutions may therefore be determined by titrating against metallic zinc or standard zinc solutions and then making use of the ratio $3\text{Zn}:2\text{Fe}(\text{CN})_6$.

The next step in the determination of the composition of the indium ferrocyanide precipitate was to prepare pure indium by electrolysis on a rotating platinum cathode from a carefully purified solution of indium sulfate. The cathode coated with indium metal was washed, dried in an atmosphere of hydrogen at 110° and weighed. The sample taken for a titration was obtained by treating the electrode with 1-2 cc. of 12 *N* hydrochloric acid, washing it, drying and weighing again. This indium chloride solution was diluted to approximately 300 cc. and titrated as usual. The results of these titrations of solutions of weighed quantities of indium metal are given in Table II.

TABLE II
TITRATION OF METALLIC INDIUM AGAINST POTASSIUM FERROCYANIDE OF KNOWN MOLALITY

Milli atoms of indium	Milli moles of $\text{K}_4\text{Fe}(\text{CN})_6$	Ratio In $\text{Fe}(\text{CN})_6$
1.234	0.9874	1.250
1.203	.9634	1.245
3.067	2.437	1.258
0.8328	0.6653	1.252
1.486	1.187	1.251
1.670	1.335	1.254
	Average	1.252

The ratio of indium to ferrocyanide is clearly 1.25 or $5\text{In}:4\text{Fe}(\text{CN})_6$. Since the only other positive ions in the solution are potassium and hydrogen, the formula for the precipitated compound is presumably $\text{In}_5\text{K}(\text{Fe}(\text{CN})_6)_4$. The determination of this definite ratio of indium to ferrocyanide in combination with the 3 to 2 ratio of zinc to ferrocyanide found by Treadwell and Chevert makes it possible to standardize with metallic zinc the ferrocyanide solutions that are to be used for indium titrations. The availability of pure zinc metal as compared with indium metal makes this method of standardization convenient.

Summary

A method of analyzing indium solutions by titrating with potassium ferrocyanide and determining the end-point potentiometrically has been described. The accuracy of the end-point is estimated at one or two-tenths of a per cent.

The precipitate formed between potassium ferrocyanide and indium solutions has been shown to be definite under the conditions described. In titrations depending upon the electrolyte present, any such small errors would tend to cancel out with the subsequent indium titration.

and to contain indium and ferrocyanide in the ratio $5\text{In} : 4\text{Fe}(\text{CN})_6$ (within 0.2%). The formula of the precipitate is therefore presumably $\text{In}_5\text{K}(\text{Fe}(\text{CN})_6)_4$. The determination of the ratio of indium to ferrocyanide in this compound permits using metallic zinc for standardizing the ferrocyanide solution, since the composition of the zinc ferrocyanide precipitate has been determined.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 150]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN THORIUM OXIDE AND CARBON

BY C. H. PRESCOTT, JR. AND W. B. HINCKE

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Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria, using the same general methods and apparatus that have been more completely described in an article on zirconium oxide and carbon.¹ Many facilities have been added to increase the precision and improve the physical conditions of the work. The equilibrium measurements have been carried on up to a temperature of 2500°K . As a result of the higher temperatures now employed many new sources of difficulty and error have been encountered, necessitating a complete study of the temperature corrections for the deviations in behavior of the carbon furnace from that of an ideal black body. It has not been possible to make the carbon elements strictly reproducible but, in spite of the elevated temperature, results have been obtained comparable in precision to the previous work under more moderate conditions.

Previous work on the reduction of thorium oxide by carbon is that of Troost² and of Moissan and Étard.³ Impure thorium metal can be obtained, but with excess of carbon the carbide, ThC_2 , is formed. This is a yellow, crystalline compound that yields a wide variety of hydrocarbons on hydrolysis with water. These have been studied in detail by Lebeau and Damiens.⁴

Acknowledgment is due to Dr. W. E. Forsythe of the Nela Research Laboratory for assistance with the pyrometry.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

¹ C. H. Prescott, Jr., *THIS JOURNAL*, 48, 2534 (1926).

² Troost, *Compt. rend.*, 116, 1229 (1893).

³ Moissan and Étard, *ibid.*, 122, 576 (1896).

⁴ Lebeau and Damiens, *Compt. rend.*, 156, 1987 (1913).

The Temperature Measurements

The temperature was measured with an optical pyrometer of the disappearing filament type made in the laboratory shop after a design by Forsythe.⁶ Two thicknesses of Corning red glass were used for a monochromatic screen and absorption screens were used of noviweld glass, shade six and shade eight. These were calibrated through the courtesy of the Nela Research Laboratory. The effective wave length of the red screen was approximately 0.660μ . The pyrometer was calibrated against a standard ribbon filament tungsten lamp, also obtained from the Nela Research Laboratory.

Corrections for the emissive power of carbon were obtained on six different furnaces mounted in furnace bulb No. 1.¹ Each had three holes 0.38 mm. in diameter in its wall, 120° apart around its circumference, and 1.6 mm. apart along its axis at the center where the temperature was most uniform. The hole served as an experimental black body and a comparison of the temperature (T) measured there with the apparent temperature (S) of the adjacent wall afforded a determination of the effective emissive power (ϵ) of the carbon. This is calculated from the Wien radiation law by the formula

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda \ln \epsilon}{c_2}$$

Here λ is the effective wave length of the red screen and c_2 is $14,330\mu$ degrees. This effective emissive power is the quantity giving the actual correction between true and observed temperature as required for the equilibrium determinations. The data obtained on the emissive power from 1250 to 2700°K . are best summarized by the relation $\epsilon = 0.930 - 4.17 \cdot 10^{-5}T$.

It was found that the inside and outside surfaces of several of the furnaces were not quite concentric; there was considerable temperature gradient along the furnace except at the exact center; there were progressive changes in the surface due to volatilization, especially at the higher temperatures. As a result there were errors in the calculated emissive power, increasing with the temperature, corresponding to a variation in the temperature as great as 25° from the mean at 2700°K . To balance the errors as much as possible, equal numbers of determinations were made on each of the three holes on each furnace, and a mean square solution made of all the data.

Apparatus and Procedure

The main features of the apparatus and general procedure are the same as already described in connection with the work on zirconium. The furnace is a small tube of Acheson graphite 0.318 cm. in diameter at the central section, with a 0.05cm. wall.

⁶ Forsythe, *Astrophys. J.*, **43**, 295 (1916).

The detail of the furnace and its mounting in furnace bulb No. 2 are shown in Fig. 1. For the equilibrium measurements the furnace was loaded with a small pellet of compressed thorium dioxide and graphite and connected to the apparatus in a thermostat at 35° as shown in Fig. 2. The pressure of carbon monoxide was measured on a mercury manometer and the temperature measured by sighting the pyrometer at the center of the furnace through a window in the thermostat. The transmission of this system of two windows with water between was measured and found to be 78.7%.

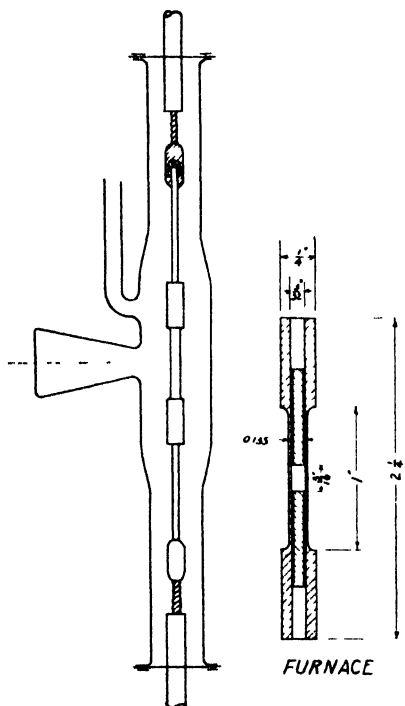


Fig. 1.—Furnace bulb No. 2.

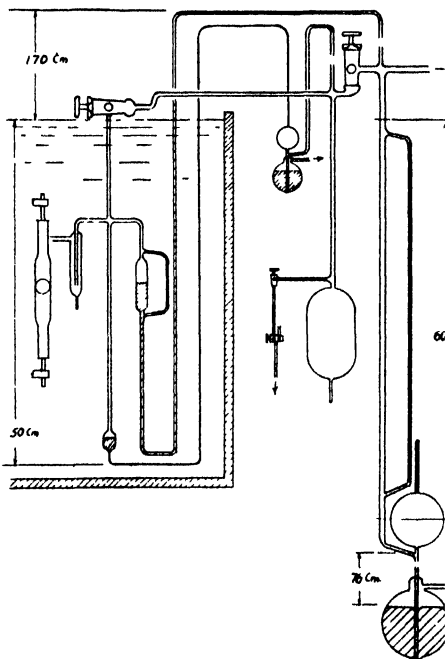


Fig. 2.—Diagram of apparatus for high temperature equilibria.

The power was drawn from a battery of sixty 150-ampere-hour storage cells. At 2500°K . six cells were connected in series and ten in parallel, the current being about 110 amperes. The current was measured and controlled by a Leeds and Northrup Type K potentiometer, using the potential drop across a 0.0034-ohm resistance. At constant current the temperature was very steady throughout a run, so only a few measurements were necessary. The pyrometer current was measured on the same potentiometer from the potential drop across a 1-ohm standard resistance.

Two observers were required, one to make pyrometer settings, read the manometer and perform manipulations, the other to read the potentiometer, regulate the furnace current and record data.

Most of the runs were from fifteen to forty minutes in length; each constituted a determination of the rate of change of pressure at a definite temperature and pressure. As it was more convenient to vary the temperature, a series of runs was made at approximately the same pressure, from which the equilibrium temperature could be estimated by interpolation.

It was found advisable to subject each furnace to a preliminary baking out at 2400°K. under a pressure of two atmospheres (above the equilibrium pressure of the reaction) to drive off adsorbed oxygen.

The product of the reaction was a yellow, microcrystalline aggregate smelling strongly of acetylene immediately upon removal from the furnace. Within a few hours it hydrolyzed to a buff-colored powder, with considerable increase in volume, even when kept over phosphorus pentoxide.

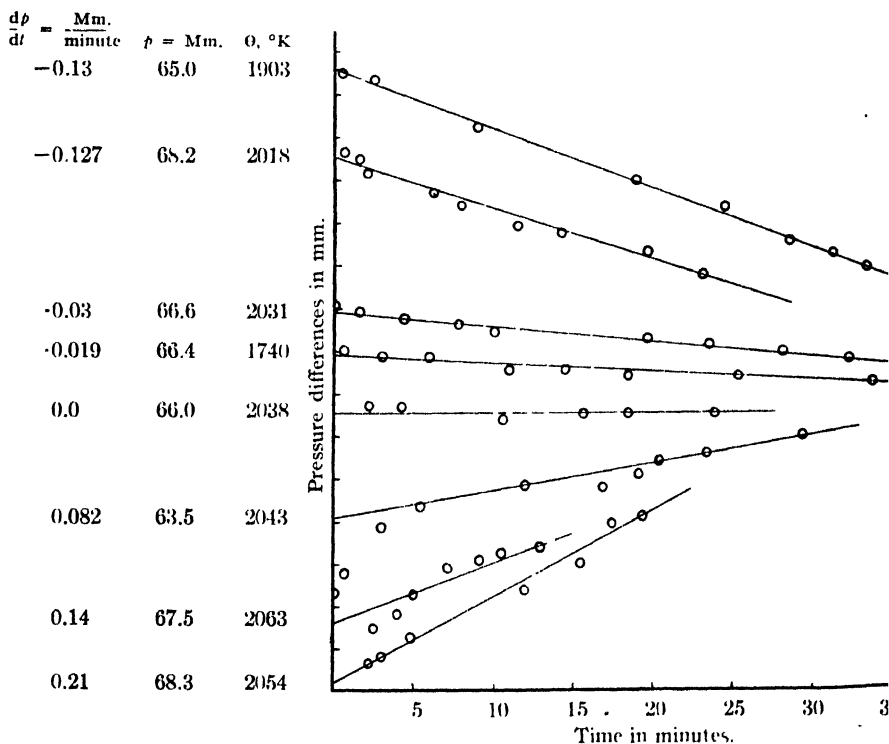


Fig. 3.--Original data at 6.54 cm.

Results of the Equilibrium Measurements

In working up the data the pressures during a run were plotted against the time. The slope of the best straight line gave the rate for the run. Rates at the same pressure were then plotted against the observed temperature (uncorrected). Each of the family of curves so obtained shows the combined influence of two factors, the deviation from equilibrium conditions and an exponential rise in the rate of reaction with temperature. The rate of pressure increase rises enormously with temperature above the equilibrium conditions, decreases to zero at equilibrium and becomes negative as the temperature is reduced, returning to zero as the temperature falls below 1800°K. The intercept of this curve was taken as the ob-

served equilibrium temperature (Figs. 3, 4 and 5 are given as typical examples). To this were added corrections for the transmission of the

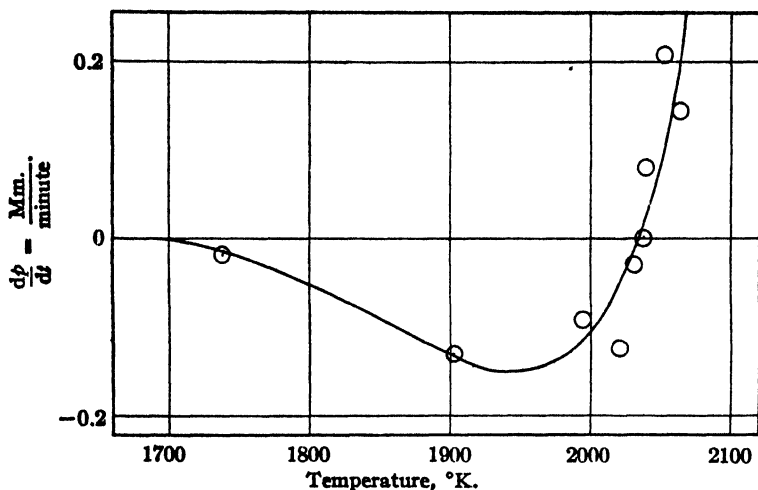


Fig. 4.

window and for the emissivity of graphite to give the true temperature. The logarithms of the pressures in atmospheres were then plotted against

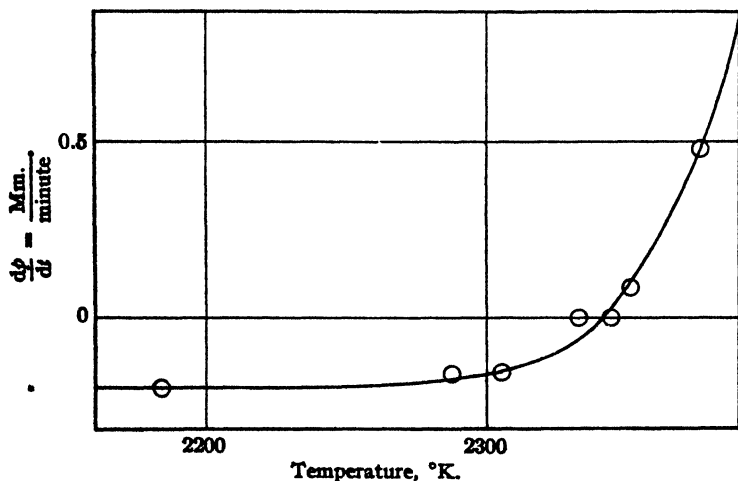


Fig. 5.

the reciprocals of the true equilibrium temperatures (Fig. 6). Since the change in the heat of reaction is small, these should fall on a straight

line and a least square solution was made for the most probable values of its constants. The largest deviation corresponds to an error of 40% in the pressure, which is easily accounted for by the imperfections of the furnace described in connection with the emissivity measurements. The final relation between equilibrium pressure in atmospheres and the true temperature in degrees Kelvin is given by the equation,

$$\text{Log } p = 8.069 - 19,325/T$$

The true temperatures and pressures are plotted in Fig. 7 in the original coördinates where the curve corresponds to the line in Fig. 6. These

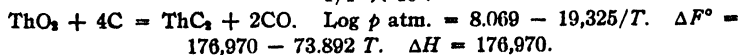
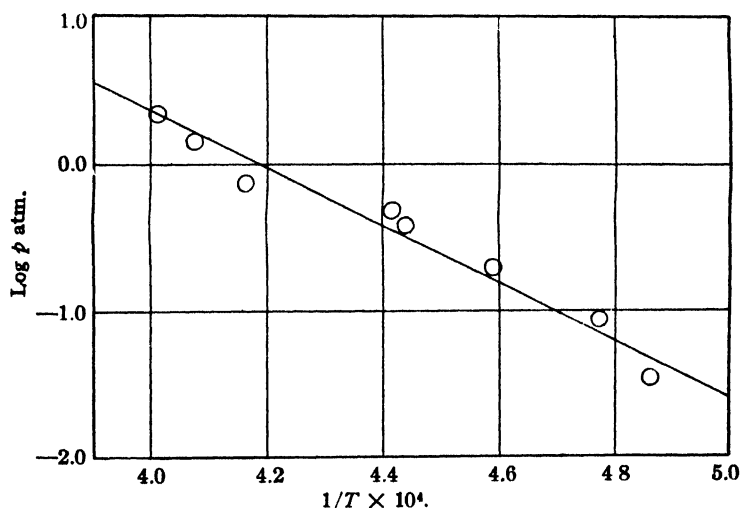


Fig. 6.

values are tabulated in Table I where θ is the observed temperature, S is the brightness temperature of carbon (corrected for the transmission of the window), T is the true temperature (corrected for the emissivity of carbon) and p is the pressure.

TABLE I
EQUILIBRIUM PRESSURES AND TEMPERATURES

θ , °K.	S , °K.	T , °K.	p , atm.
2377	2441	2494	2.17
2341	2403	2454	1.39
2293	2352	2402	0.752
2170	2223	2265	.480
2158	2210	2252	.380
2092	2141	2179	.192
2035	2082	2117	.0861
1980	2024	2057	.0345

The reaction was so rapid, especially at the higher temperatures, that the interface was not closely comparable from one run to the next, producing considerable variation in the rates. Also, when near equilibrium, the rate would fall off after a couple of runs, probably due to a sintering effect increasing the particle size. It was particularly noticeable that on the reversal of the reaction after a large rate the initial rate was larger than anticipated until the newly formed material was exhausted. There were two very striking observations leading to the above explanations. While determining the equilibrium at 2500°K. the current was momentarily raised enough to fuse the pellet. No further reaction was detect-

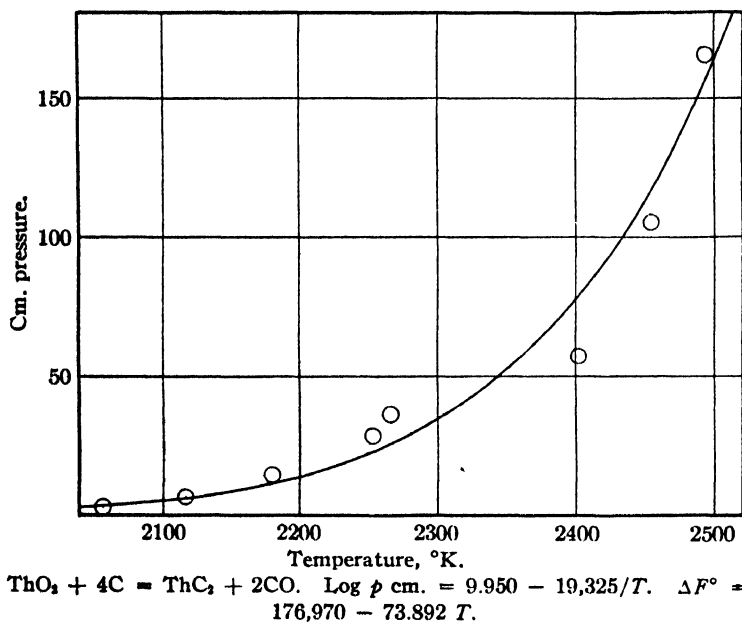


Fig. 7.

able. One series of runs at low temperature was made on a pellet of exact proportions to produce ThC_2 . The forward rates were normal, but no reverse rates were obtained until the pressure was increased many fold, when an extremely slow reverse rate was observed under conditions where previously the reverse reaction went to completion before any readings could be taken. The published data were obtained on pellets containing an excess of oxide to separate the particles of carbide formed, the proportions corresponding to the hypothetical formation of ThC .

Besides the preliminary data which were not so correlated that an equilibrium temperature could be interpolated, one complete series of runs was discarded in which the rates were very small and erratic. It was found that the reverse reaction had gone to completion before the

readings were taken. On running the reaction ahead for a pressure increase of two centimeters a normal series of runs was obtained with no other change.

The Melting Point of Thorium Carbide

The behavior of a melted pellet has been partly described in the preceding paragraph. Besides the cessation of reaction, it was remarked that the furnace current had increased at the same setting of the control resistances. After regulating the current it was found that the temperature had dropped greatly. On removal it was seen that the pellet had wet the furnace wall and presumably short circuited the central segment. This suggested a method of determining the melting point of the carbide.

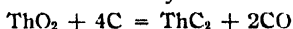
A pellet of proportions to yield ThC_2 was mounted in furnace bulb No. 1. It was run, *in vacuo*, at 2100°K . for an hour and a half so as to form the carbide. Carbon monoxide was then admitted to one atmosphere pressure and the temperature raised to 2500°K . The temperature was raised by approximately ten degree steps. At each setting the current was held constant and voltage read across the furnace bulb terminals before and after a series of pyrometer readings. The voltage increased slightly due to the volatilization of the furnace.

At a current of 120.5 amperes the true temperature was 2773°K . The voltage dropped from 7.783 volts to 7.772. Another series of readings showed that the temperature was dropping, and in a few minutes the temperature had dropped 50° , the potential 0.1 volt, and both were changing rapidly.

Upon removal, one-half of the pellet was found melted and the other was a microcrystalline aggregate as in previous preparations at lower temperatures. The preparation was probably reasonably pure at the moment of fusion, so the above value of 2773°K . is not far off.

Thermodynamic Calculations

The chemical reaction is undoubtedly



We may now proceed to calculate the free-energy increase (ΔF) and the heat-content increase (ΔH) attending this reaction when the carbon monoxide pressure is one atmosphere.

The value of ΔF may be derived from the equilibrium pressure p by the familiar thermodynamic equation $\Delta F^\circ = -RT \ln K$, where $K = p^2$. From the determinations of the equilibrium pressure p tabulated in Table I we thus obtain the values given in Table II.

TABLE II

FREE-ENERGY INCREASE ATTENDING THE REACTION

Temp., T , $^\circ\text{K}$.	2494	2454	2402	2265	2252	2179	2117	2057
ΔF° , cal.	-7685	-3224	2723	6612	8666	14301	20660	27543

From the expression for $\log_{10} p$ derived in the same section we similarly obtain the relations, $\Delta F^\circ = 176,970 - 73.89 T$, and $\Delta H = 176,970$ calories. At 2395°K . the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

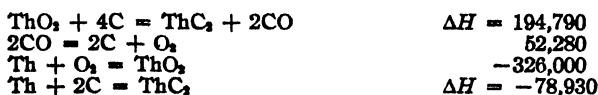
The molal heat capacities, C_p , of graphite and carbon monoxide were taken from Lewis and Randall,⁶ and those of thorium oxide and carbide estimated from Kopp's law according to the scheme given in Noyes and Sherrill.⁷

For C	$C_p = 1.1 + 0.0048T - 0.0000012T^2$
For CO	$C_p = 6.50 + 0.0010T$
For ThO_2	$C_p = 14.2$
For ThC_2	$C_p = 9.8$

From the above-mentioned heat of reaction and the zero value of the free-energy change at 2395°K . the following equations are obtained and from them by extrapolation the following values at room temperature.

$$\begin{aligned}\Delta H &= 194,261 + 4.2T - 0.0086T^2 + 0.0000016T^3 \\ \Delta F^\circ &= 194,261 - 4.2T \ln T + 0.0086T^2 - 0.0000008T^3 - 64.438T \\ \Delta H_{298} &= 194,790 \text{ cal.}; \Delta F^\circ_{298} = 188,660 \text{ cal.}\end{aligned}$$

Combining this heat of reaction with the heat of formation of carbon monoxide,⁸ and the heat of formation of thorium oxide,⁸ permits a calculation of the heat of formation of thorium carbide.



Summary

The chemical equilibrium between thorium oxide, graphite, thorium carbide and carbon monoxide has been determined at temperatures from 2000 to 2500°K ., and at pressures from two centimeters to two atmospheres.

Temperatures were measured with an optical pyrometer. The furnace was a graphite tube 0.318 cm. in diameter with a 0.05cm. wall supported on tungsten rods and enclosed in Pyrex glass. The pressures were read on a mercury manometer. The enclosed gas space was about 100 cc. and was all below the water level of a thermostat at 35° .

Experiments were made on compressed pellets of thorium oxide and graphite. The procedure was to determine at a series of temperatures and pressures the rate of change of pressure with the time. From a series of such experiments at a single pressure and different temperatures the equilibrium temperature was estimated.

⁶ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 89, 569, 576.

⁷ Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, 1922, p. 93.

⁸ Von Wartenberg, *Z. Elektrochem.*, 15, 869 (1909).

The increases in free-energy and heat-content that would attend this reaction between 2000 and 2500°K. at one atmosphere were found to be those given by the equations $\Delta F^\circ = 176,970 - 73.89T$, and $\Delta H = 176,970$ calories.

At 2395°K. the free-energy change becomes zero and the actual equilibrium pressure is one atmosphere.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No 151]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN ALUMINUM OXIDE AND CARBON

BY C. H. PRESCOTT, JR.¹ AND W. B. HINCKE

RECEIVED AUGUST 12, 1927

PUBLISHED NOVEMBER 5, 1927

Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria, using the same apparatus and procedure that have already been applied to reactions between zirconium oxide and carbon,² and thorium oxide and carbon.³ The extraordinary stability of the oxides and carbides of zirconium and thorium at incandescent temperatures has rendered them very fortunate objects of study. Though the results are no less definite, the volatility of aluminum carbide and its consequent tendency to depart from the reaction area have limited the precision attainable in the study of the equilibrium between aluminum oxide and carbon.

The first reliable study of aluminum carbide is that of Moissan⁴ who prepared it from its elements in the electric furnace. He found it to be a yellow, crystalline compound of composition corresponding to the formula Al_4C_3 , yielding methane on hydrolysis. Askenasy⁵ and his associates have shown that mixtures of carbide and metallic aluminum may be obtained by reduction of the oxide with carbon. Fraenkel⁶ has shown that the carbide is formed at more moderate temperatures. Ruff⁷ has made approximate measurements on the vapor pressure of aluminum carbide, finding that at 2200° the carbide melts and is in equilibrium with liquid aluminum and carbon and with a vapor at 400 mm.

¹ National Research Fellow in Chemistry.

² C. H. Prescott, Jr., *THIS JOURNAL*, **48**, 2534 (1926).

³ Prescott and Hincke, *ibid.*, **49**, 2744 (1927).

⁴ Moissan, *Compt. rend.*, (II) **119**, 15 (1894).

⁵ Askenasy, Jarkowsky and Waniczek, *Z. Electrochem.*, **14**, 811 (1908). Askenasy and Lebedeff, *Z. Elektrochem.*, **16**, 559 (1910).

⁶ Fraenkel, *ibid.*, **19**, 362 (1913).

⁷ Ruff, *ibid.*, **24**, 157 (1918).

pressure containing about equal parts of aluminum and aluminum carbide. Ruff⁸ has also determined the melting point of aluminum oxide as between 1965 and 2065°, stating that the oxide is volatile at about 1900°.

The present investigation has been aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Apparatus and Procedure

The apparatus and general procedure have already been completely described in references (2) and (3).

Most of the runs were from ten to thirty-five minutes in length; each constituted a determination of the rate of change of pressure in the furnace bulb at a definite temperature and pressure. As it was more convenient to vary the temperature, a series of runs was made at approximately the same pressure, from which the equilibrium temperature could be estimated by interpolation. This procedure was followed on furnaces A to E. In the hope that a different procedure would give better curves for the interpolation, series were made at constant temperature and different pressures on furnaces F to H.

In preliminary experiments it was found that extremely intimate contact was necessary in order to prepare the carbide, so all subsequent work was done on pellets made by thoroughly grinding graphite and an excess of aluminum oxide in ether and just enough Nujol (a pure paraffin oil) to bind the sample when compressed in a pellet press. The excess oxide was to help make up for losses of aluminum by vaporization.

Forward rates with evolution of carbon monoxide were invariably accompanied by a cream-colored deposit on the walls of the glass tube enclosing the furnace, and a black or dark brown deposit at pressures below 5 cm. Reverse rates were frequently terminated by exhaustion of carbide, and more had to be generated by running at higher temperature or lower pressure before another reverse rate could be obtained. Furnaces A, B and C were run till no further reaction could be obtained. The residue of the charge was found to be a small quantity of graphite which ignited completely on a platinum foil. The remaining furnaces were run for but one equilibrium determination apiece; their charges always showed some residue of white oxide on ignition, and in most cases some yellow carbide was to be seen in the charge.

To remove absorbed oxygen from the graphite furnace, each was subjected to a preliminary baking for an hour at about 2050°K. under a pressure of 2.5 atmospheres of carbon monoxide (above the equilibrium pressure of the reaction). During this treatment a slight white deposit appeared which was probably aluminum oxide.

In a preliminary preparation given fifteen minutes at 2000°K., *in vacuo*,

⁸ Ruff, *Ber.*, **43**, 1571 (1910).

a preparation of yellow carbide mixed with graphite was obtained which gave a considerable evolution of hydrocarbon fumes on treatment with sodium hydroxide.

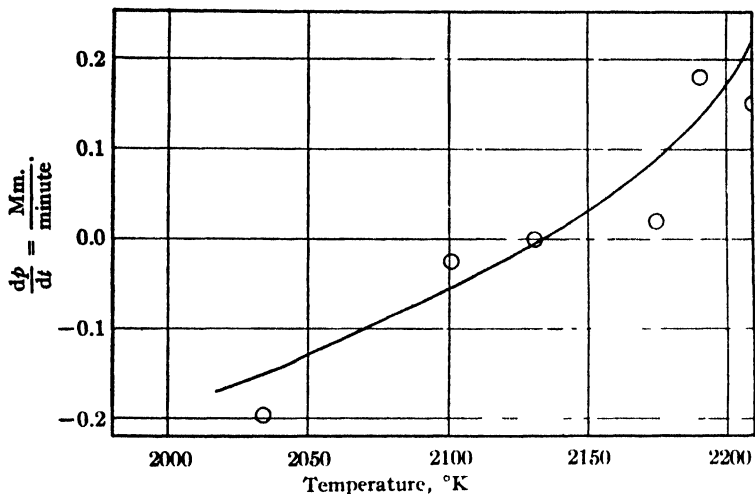


Fig. 1.—Furnace E. $\theta = 2134$. $T = 2224^{\circ}\text{K}$. $p = 4408$ atm.

Both the black and the white material deposited during the carbide formation dissolved completely in both hydrochloric acid and sodium

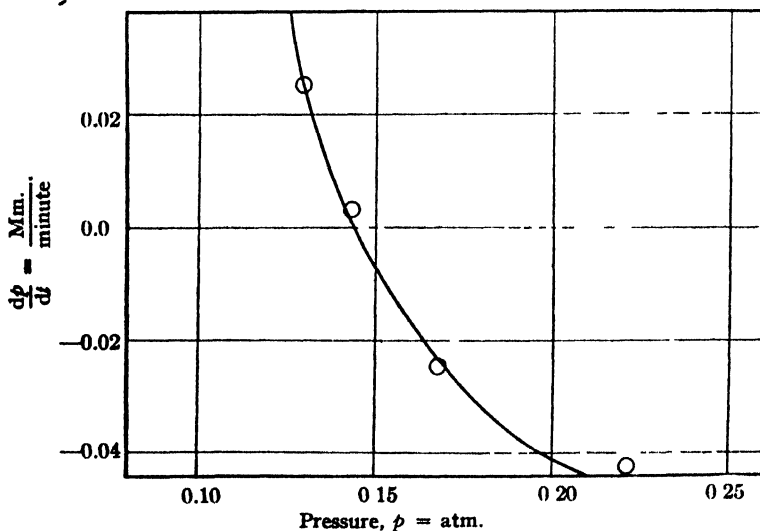


Fig. 2.—Furnace F. $T = 2071^{\circ}\text{K}$. $p = 141$ atm

hydroxide and gave characteristic tests for aluminum. On ignition the cream-colored material flashed and turned black. Both deposits

gave white oxide on continued ignition. Since it is reported⁹ that metallic aluminum reacts with carbon monoxide to give a mixture of carbide and oxide, and the black deposit appeared at low pressures where the rate of reaction was greatest, the black deposit was probably aluminum and the cream-colored aluminum carbide.

Results of the Equilibrium Measurements

The observed rates of change of pressure in the furnace bulb certainly give limits in almost all cases to the possible values of the equilibrium conditions, but due to the radical changes in the pellet and solid interface from one run to the next, the graphical interpolation is attended with considerable uncertainty. Figs. 1 and 2 are given as typical examples of the plots of rate of change of pressure.

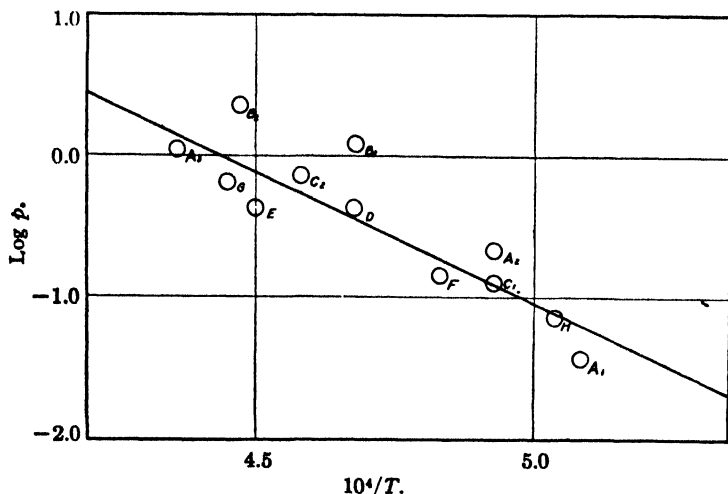


Fig. 3.

In Fig. 3, the logarithms of the equilibrium pressures in atmospheres are plotted against the reciprocals of the true temperatures. Since the change in the heat of reaction is small, these points should fall on a straight line and a least square solution was made for its constants. As the earlier values were less certain, and, in particular, since determining more than one equilibrium on each furnace was inadvisable, equal weight was given to the values obtained on each furnace, that is, A_1 , A_2 and A_3 were weighted $1/3$ each, and B_1 , B_2 , C_1 and C_2 , $1/2$ each. The final relation between the equilibrium pressure in atmospheres and the true temperature in degrees Kelvin is given in the equation

$$\text{Log } p = 8.21 - 18,480/T$$

⁹ Pring, *J. Chem. Soc.*, 87, 1530 (1905).

The true temperatures and pressures are plotted in Fig. 4 in the original coördinates where the curve corresponds to the line in Fig. 3. These values are tabulated in Table I where θ is the observed temperature, S is the

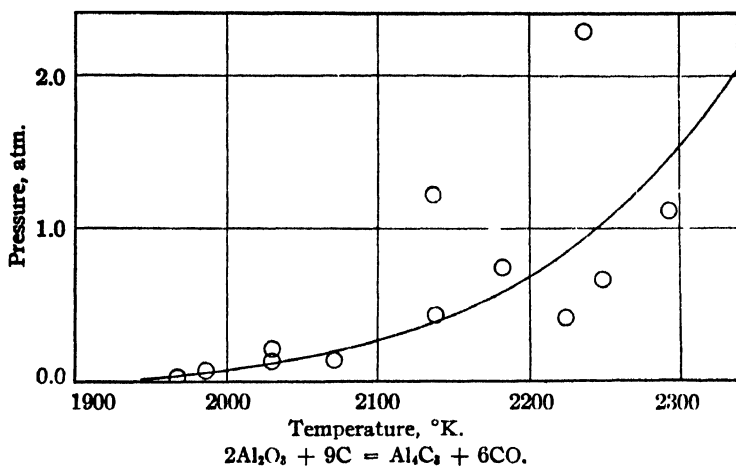


Fig. 4.—Equilibrium pressures and temperatures

brightness temperature of carbon (corrected for the transmission of the window), T is the true temperature (corrected for the emissivity of carbon) and p is the pressure.

TABLE I

EQUILIBRIUM PRESSURES AND TEMPERATURES				
Detn.	θ , °K.	S , °K.	T , °K.	p , atm
A ₁	1898	1938	1967	0.0376
A ₂	1956	1999	2030	.2193
A ₃	2196	2250	2293	1.122
B ₁	2054	2101	2137	1.222
B ₂	2145	2197	2237	2.288
C ₁	1956	1999	2030	0.1308
C ₂	2101	2146	2183	.746
D	2055	2102	2138	.484
E	2134	2185	2224	.441
F	1994	2039	2071	.144
G	2156	2208	2248	.668
H	1908	1956	1987	.0731

Thermodynamic Calculations

The equation expressing the chemical reaction is undoubtedly



The value of ΔF° , the free-energy increases attending this reaction, may be derived from the familiar thermodynamic equation, $\Delta F^\circ = -RT \ln K$, where $K = p^6$. From the determinations of the equilibrium pressure p tabulated in Table I we thus obtain the values given in Table II.

TABLE II
 FREE ENERGY INCREASE

Detn.	Temp. T, °K.	ΔF°	Detn.	Temp. T, °K.	ΔF°
A ₁	1967	-76,990	C ₂	2183	-7634
A ₂	2030	-36,750	D	2138	-21,020
A ₃	2293	3150	E	2224	-21,740
B ₁	2137	5112	F	2071	-47,880
B ₂	2237	22,090	G	2248	-10,808
C ₁	2030	-49,270	H	1987	-62,020

From the expression for $\log_{10} p$ derived in the same section we similarly obtain the relations $\Delta F^\circ = 507,760 - 225.6T$, and $\Delta H = 507,760$ calories. At 2251°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

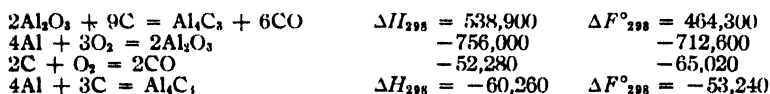
The molal heat capacities, C_p , of graphite and carbon monoxide were taken from Lewis and Randall,¹⁰ and those of aluminum oxide and carbide from Kopp's law according to the scheme given in Noyes and Sherrill,¹¹ as giving a reasonable approximation at high temperatures.

$$\begin{array}{ll}
 \text{For C} & C_p = 1.1 + 0.00487T - 0.00000127T^2 \\
 \text{For CO} & C_p = 6.50 + 0.00107T \\
 \text{For Al}_2\text{O}_3 & C_p = 24.4 \\
 \text{For Al}_4\text{C}_3 & C_p = 30.2
 \end{array}$$

From the above-mentioned heat of reaction and the zero value of the free-energy change at 2251°K., the following equations are obtained and from them by extrapolation the following values at room temperature,

$$\begin{aligned}
 \Delta H &= 537,310 + 10.50T - 0.0186T^2 + 0.00000367T^3 \\
 \Delta F^\circ &= 537,310 - 10.50T \ln T + 0.0186T^2 - 0.00000187T^3 - 190.39T \\
 \Delta H_{298} &= 538,900 \text{ cal.} \\
 \Delta F^\circ_{298} &= 464,300
 \end{aligned}$$

Using these values and the values for the formation of aluminum oxide given by Parks and Kelley,¹² and values for the formation of carbon monoxide from Lewis and Randall,¹⁰ values may be calculated for the formation of aluminum carbide from its elements.



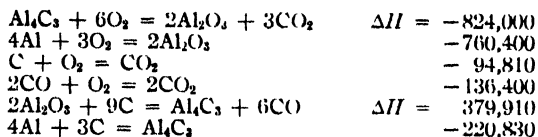
From heats of combustion determined by Berthelot,¹³ the heat of reaction for the reduction of aluminum oxide to carbide may be calculated, as well as the heat of formation of aluminum carbide.

¹⁰ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 80, 560, 576.

¹¹ Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, 1922, p. 93.

¹² Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

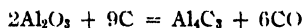
¹³ Berthelot, *Ann. Chim. Phys.*, [7] **22**, 470 (1901); [7] **22**, 479 (1901); Berthelot and Petit, *ibid.*, [6] **18**, 98 (1889); Berthelot and Matignon, *ibid.*, [6] **30**, 555 (1893).



The first value is in disagreement with the results of the present work by 160,000 calories. However, the determination of the heat of reaction is not so accurate as those for the free energy, and the slope of the line in Fig. 3 could be reduced by one-third without very serious prejudice to the data; but Berthelot himself remarked that the heat of formation of the carbide seemed abnormally large. The presence of oxide in his carbide might account for the discrepancy.

Summary

Determinations have been made of the chemical equilibrium for the reaction



The increases in free energy and heat content that would attend this reaction between 2000 and 2300°K. and one atmosphere pressure were found to be those given by the equations, $\Delta F^\circ = 507,760 - 225.6T$ and $\Delta H = 507,760$ calories. At 2251°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-CARBONDISULFIDE. III. BEHAVIOR OF AZIDO-CARBONDISULFIDE TOWARD CHLORINE, BROMINE AND IODINE¹

By WM. HOWLETT GARDNER AND A. W. BROWNE

RECEIVED AUGUST 12, 1927

PUBLISHED NOVEMBER 5, 1927

Azido-carbondisulfide may not inappropriately be designated as a *universal reagent* in the sense in which water has been termed a "universal solvent." Its reactivity toward acids and alkalies, toward oxidizing and reducing agents, toward certain metals and non-metals, toward water and ammonia, and apparently even toward certain organic solvents, together with its tendency to undergo an extremely regular autocatalytic decomposition at room temperature, seems to entitle this substance to characterization as an almost unique reagent.

In connection with the distinctly halogenoid character of azido-carbon-

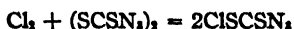
¹ For the earlier articles of this series see (a) Browne, Hoel, Smith and Swezey, *THIS JOURNAL*, **45**, 2541 (1923); (b) Wilcoxon, McKinney and Browne, *ibid.*, **47**, 1916 (1925). The current article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by William Howlett Gardner in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

disulfide the question has arisen as to whether this reagent may be caused to react with any of the other halogenoids, or with any of the halogens, forming inter-halogenoid or halogen-halogenoid compounds analogous to the inter-halogen compounds. The latter part of this question has been answered in the present investigation.

From the list of inter-halogen compounds theoretically capable of existence as definite chemical individuals, bromine trifluoride,² iodine pentafluoride,^{3,3c} iodine monochloride and trichloride⁴ and iodine monobromide⁵ have been prepared. Among the halogen-halogenoid compounds are chlorazide,⁶ bromazide⁷ and iodazide,⁸ cyanogen chloride,⁹ bromide,¹⁰ and iodide;¹¹ and thiocyanogen monochloride and trichloride.¹² The inter-halogenoids include cyanazide,¹³ cyanogen thiocyanate,¹⁴ and cyanogen selenocyanate.¹⁵

Behavior of Azido-carbondisulfide toward Chlorine

When dry azido-carbondisulfide is brought into contact at room temperature with chlorine, either in the gaseous form or in concentrated aqueous solution, a violent explosion occurs at once. It is very probable that the initial reaction consists in an exothermic union of chlorine with the halogenoid, resulting in the transitory, superficial formation of a chlorine azido-dithiocarbonate in accordance with the equation



Since a rise of temperature of but a few degrees suffices to initiate the explosion of azido-carbondisulfide, however, the reaction does not proceed

² (a) Pridcaux, *Proc. Chem. Soc.*, 21, 240 (1905); (b) 22, 19 (1906); (c) *J. Chem. Soc.*, 89, 316 (1906); (d) Lebeau, *Compt. rend.*, 141, 1018 (1905); (e) *Bull. soc. chim.*, [3] 35, 148 (1906); (f) *Ann. chim. phys.*, [8] 9, 241 (1906).

³ (a) Gore, *Phil. Mag.*, (4) 41, 309 (1871).

⁴ (a) Stortenbecker, *Z. physik. Chem.*, 3, 11 (1889); (b) *Rec. trav. chim.*, 7, 152 (1888).

⁵ Terwogt, *Z. anorg. Chem.*, 47, 203 (1905).

⁶ Raschig, *Ber.*, 41, 4194 (1908). Qualitative evidence only has been adduced as yet in support of the existence of this compound.

⁷ Spencer, *J. Chem. Soc.*, 127, 216 (1925).

⁸ (a) Hantzsch, *Ber.*, 33, 522 (1900). See also Gutmann, *ibid.*, 57, 1956 (1924).

⁹ (a) Berthollet, *Ann. chim.*, [1] 1, 30 (1789); (b) Gay Lussac, *ibid.*, [1] 95, 156-231 (1815); (c) Serullas, *Ann. chim. phys.*, [2] 35, 291 (1827).

¹⁰ Serullas, *ibid.*, [2] 34, 95 (1827).

¹¹ Serullas, *ibid.*, [2] 27, 184 (1824).

¹² (a) Kaufmann and Liepe, *Ber.*, 57, 923 (1924); (b) Lecher and Joseph, *ibid.*, 59, 2803 (1926).

¹³ Darzens, *Compt. rend.*, 154, 1232 (1912).

¹⁴ (a) Linnermann, *Ann.*, 120, 36 (1861); (b) Söderbäck, *ibid.*, 419, 217 (1919); (c) Schneider, *J. prakt. Chem.*, [2] 32, 187 (1885).

¹⁵ (a) Verneuil, *Ann. chim. phys.*, [6] 9, 326 (1886); (b) Kaufmann and Kögler, *Ber.*, 59, 178 (1926).

far before the reacting mass explodes, yielding the usual products of decomposition of the halogenoid.^{1a}

By passing chlorine gas through an anhydrous solution of azido-carbon-disulfide in chloroform at -15° no evidence of decomposition is obtained, unless the chlorine is introduced in large excess. After the unused chlorine has been removed by means of a current of dry air, the solution is found to have acquired a characteristic pungent odor and a white solid appears after vaporization of the greater part of the solvent. Even at temperatures below -20° this undergoes gradual transformation into a viscous, yellow oil, insoluble in water and in chloroform. The vapor of this oil affects the eyes and, if inhaled, appears to act as a heart depressant. It attacks rubber, causing it to swell. Contact of the oil with the skin causes blistering. At room temperature the oil undergoes rapid decomposition with evolution of gas.

Qualitative tests indicate that the unstable yellow oil may be a chlorine compound of azido-carbondisulfide of the formula ClSCSN_3 . It has not yet been found possible to carry quantitative determinations of the compound to satisfactory completion.

Behavior of Azido-carbondisulfide toward Bromine

Attempts to prepare a bromine azido-dithiocarbonate by interaction of liquid bromine and solid azido-carbondisulfide at ordinary temperatures resulted in violent explosions. Even at temperatures slightly above the melting point of bromine, rapid decomposition was found to take place.

In organic solvents such as ethyl alcohol, acetone, ether, chloroform or carbon tetrachloride, however, the bromine color is immediately discharged by azido-carbondisulfide and no evolution of gas occurs if the solution is kept at a temperature below -5° , unless an excess of bromine is present. Evaporation of the resulting solutions at -10° by means of dry air yields a white, odorless, amorphous product which immediately turns yellow above -5° . The water extract of the white or of the yellow substance was found to contain bromides in considerable amount. The yellow solid, while not explosive, turns brownish in color slowly on standing, and rapidly when heated to 200° .

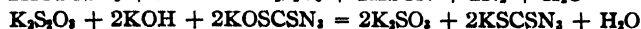
Because of the fact that solutions of azido-carbondisulfide in organic solvents after treatment with bromine solutions do not liberate iodine from potassium iodide until free bromine is present, it was found possible to titrate such solutions at -10° , using moist starch-potassium iodide paper as an outside indicator. The degree of accuracy obtainable by this method is somewhat lowered by the difficulty of judging the end-point and by the rather rapid deterioration of the bromine solutions.

With carbon tetrachloride and with ether as solvents, such titrations indicate that bromine reacts with the azido-carbondisulfide in equivalent

(1:1) ratio under the prevailing conditions. With other organic solvents varying results were obtained. In chloroform, for example, the results indicate that union takes place in a ratio smaller than 1:1. In ethyl bromide, on the other hand, no reaction at all was observed to occur.

When solutions of bromine in carbon tetrachloride, chloroform or ether were added to a suspension of silver azido-dithiocarbonate in the same liquid at -10° , the color of the bromine was at once discharged and silver bromide was formed. The colorless filtrate, like the solutions obtained by interaction of bromine and azido-carbondisulfide, showed no action upon aqueous solutions of potassium iodide, on treatment with iron filings gave no evidence of the presence of free thiocyanogen and underwent no decomposition with liberation of nitrogen below -5° . Evaporation at -10° yielded as before a white, amorphous solid apparently identical in properties and behavior with that just described.

Hydrolysis of non-aqueous solutions of bromine azido-dithiocarbonate by the action of aqueous alkalis yields solutions of the greenish-yellow color characteristic of similarly hydrolyzed azido-carbondisulfide.^{1a} The presence of both bromine ion and azido-dithiocarbonate ion was readily established. Sulfites and thiosulfates were also demonstrated to be present. The following equations express the reactions believed to occur during hydrolysis of the compound in concentrated solutions of potassium hydroxide.



Determinations of the bromine-sulfur ratio were made upon samples of bromine azido-dithiocarbonate prepared by the interaction of bromine and the silver salt in ether, carbon tetrachloride and chloroform. The results indicate that in ether the formation of a tribromo-azido-dithiocarbonate takes place, while in the other solvents a mixture of a mono-bromo and a tribromo compound is obtained.

From these results it may be inferred that the reaction between bromine and silver azido-dithiocarbonate probably occurs in accordance with either or both of the equations



Owing to the extreme instability of these compounds and their solutions, it has not yet been found possible to accomplish their complete isolation or more exact determinations of their composition.

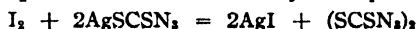
Behavior of Azido-carbondisulfide toward Iodine

Treatment of solutions of azido-carbondisulfide in carbon tetrachloride, acetone or ethyl alcohol at temperatures between 0° and -10° with dilute

solutions of iodine in these solvents does not result in a discharge of the iodine color. Unlike chlorine and bromine, therefore, iodine does not combine directly with the halogenoid under the specified conditions.

Addition of solid iodine to a concentrated aqueous solution of sodium azido-dithiocarbonate results in the immediate separation of a heavy, black oil.

Iodine reacts at once with silver azido-dithiocarbonate suspended in chloroform with formation of silver iodide. The filtrate is found to contain no iodine, however, unless this reagent has been used in excess. Therefore, no union of iodine with azido-carbondisulfide may be assumed to take place. The reaction of the substances in chloroform appears to follow a course similar to that of the reaction between iodine and sodium azido-dithiocarbonate in aqueous solution, and may be expressed by the equation



Summary

Solid azido-carbondisulfide reacts explosively with chlorine and bromine. In certain non-aqueous solvents more controllable reactions take place, with probable formation of the compounds $ClSCSN_3$ and $BrSCSN_3$. Bromine reacts with silver azido-dithiocarbonate in ether to form a tri-bromo-azido-dithiocarbonate, Br_3SCSN_3 , and in chloroform and carbon tetrachloride to form a mixture of the monobromo and tribromo compounds.

The extreme instability of these compounds precludes their exact analysis and description.

Iodine forms no compound with azido-carbondisulfide under the conditions investigated.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

HYDROGEN PEROXIDE FORMATION PHOTSENSITIZED BY MERCURY VAPOR

BY ABRAHAM LINCOLN MARSHALL

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This paper represents an effort to clear up some of the uncertain points in the photochemical combination of hydrogen and oxygen when sensitized to λ 2536.7 Å. from a cold mercury arc by means of mercury vapor. In a previous paper¹ this reaction was studied in a static system and the rates of reaction observed at that time were not at all reproducible. It was found, however, that for individual experiments the rate of reaction was best represented by the equation

$$\frac{d}{dt} (H_2O) = K \left(\frac{p_{H_2}}{p_{H_2} + p_{O_2}} \right)$$

¹ Marshall, *J. Phys. Chem.*, **30**, 34 (1926).

It was found that in practically all the experiments the reaction came to an end at a point corresponding within the experimental error to that calculated on the basis of the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$. Also, with gas mixtures of composition $2\text{H}_2 + \text{O}_2$, the rate-time curves were linear over the whole range of the reaction, which stopped abruptly when all the gas had combined. On the basis of this and a previous investigation, it was suggested by Taylor² and Marshall¹ that the reaction involved hydrogen peroxide as an intermediate product, the postulated mechanism being



with subsequent decomposition of the hydrogen peroxide vapor by a variety of processes of which one was undoubtedly the oxidation of mercury vapor.³ That this supposition was correct was shown subsequently by Marshall,⁴ who was able to remove quite large quantities of hydrogen peroxide from the reaction system by the use of a streaming method.

In the light of this result, it seemed that a further study of this reaction might bring to light some fresh factors of interest. In the original investigation liquid mercury was always present in the system and was relied on to keep the concentration of mercury vapor constant. The deposition of mercury on the walls of the reaction chamber altered the amount of light entering the system and the presence of liquid mercury made it impossible to determine the real temperature coefficient of the reaction. In the present investigation the gas mixtures were circulated by means of a glass mercury reciprocating pump (H) at a rate of about 250 liters per hour. The gas was saturated with mercury vapor at a known pressure in the saturator (A) before entering the reaction vessel (C). The temperature of the reaction system was controlled by means of the water-bath (E). Hydrogen peroxide was removed from the gas stream by means of a very efficient gas scrubbing bottle (G). A large reservoir (F) which was kept at constant temperature was introduced into the system to control the rate of pressure change which was measured on the manometer (K) and also reduce fluctuations in the manometer due to the motion of the mercury column in the pump (H), which was continually changing the volume of the system within certain limits.

Design of Arc

The design of the quartz mercury arc used in such an investigation is very important as it is essential to obtain constant illumination. In previous work the author has used the regular vertical type of Cooper-Hewitt lab.-arc, cooling the cathode end to a point about 1 cm., above the

¹ Taylor, *Trans. Faraday Soc.*, 21, 560 (1926).

² Elder and Rideal, *ibid.*, 23, 550 (1927).

⁴ Marshall, *J. Phys. Chem.*, 30, 1078 (1926).

mercury level. This, however, is unsatisfactory as it is almost impossible to keep the mercury pressure in the arc constant. An improved type of arc (B) was used in the present investigation, similar to that described by Taylor.⁵ The electrodes were made *entirely* of tungsten and it was found possible to carry currents up to 25 amperes without any blackening of the quartz walls of the arc. The arc was connected directly to a mercury

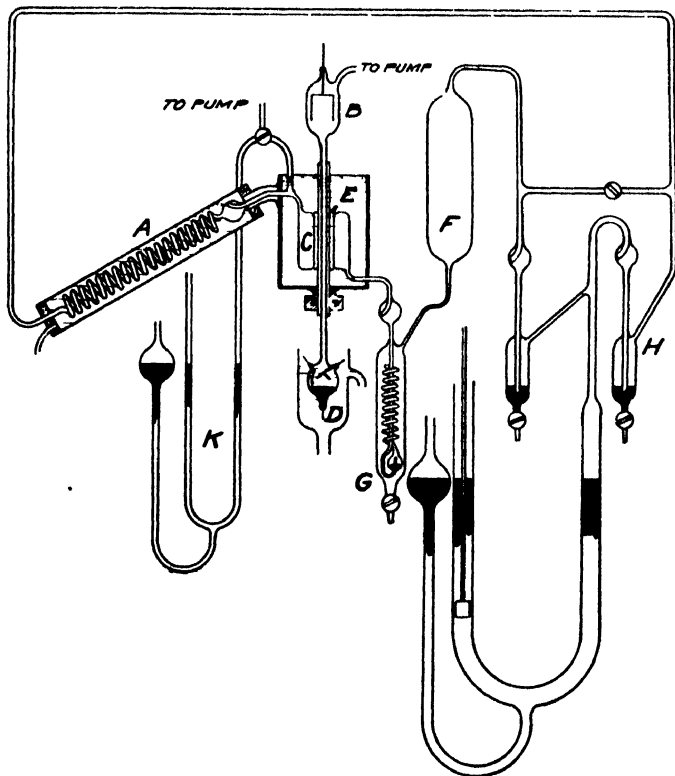


Fig. 1.

diffusion pump which was always kept in operation while the arc was running. The cathode end of the arc was immersed in water (D) which was flowing rapidly over the arc structure; the temperature was controlled within 1° by means of an electric heater. In this manner it was possible to vary the temperature over the range $13\text{--}80^\circ$.

Kinetics of Reaction

Table I gives the data for a typical experiment. In subsequent tables the rate will be given for the steady state. It was observed throughout the investigation that during the first five to ten minutes of an experiment

⁵ Taylor, *THIS JOURNAL*, **48**, 2844 (1926).

the rate was gradually accelerating to a constant value characteristic for the conditions under investigation. It was thought that this might be due to temperature changes in the system caused by heating from the arc and to the fact that the arc has to operate for some time before reaching a steady state.

TABLE I
DATA FOR TYPICAL EXPERIMENT

Temperature of Hg in arc, 30°; temperature of reaction chamber, 67°; gas saturated with Hg vapor at 50°; p_{H_2} , 520 mm.; p_{O_2} , 212 mm.; arc current, 15 amps.

Time	Press., mm.	Δp , mm./min.
0	165	
2	186	10.5
4	215	14.5
5	249	17.0
8	282	16.5
10	318	18.0
13	376	19.4
15	415	19.5
17	454	19.5
19	496	21.0
21	541	22.5
23	593	26.0
Finish	608	

The last column gives the rate of pressure change in mm. per minute.

In this experiment 410 cc. of H_2O_2 gas was formed. Since the total pressure change was 443 mm., the amount of hydrogen peroxide formed would correspond to a volume for the apparatus of 1570 cc. The estimated volume was 1500 cc.; no measurement of this was made, however, as the reservoir was destroyed by an explosion before the experiments were completed. It is certain, however, that the main product of the reaction is hydrogen peroxide.

In Table II are given the data for a series of experiments varying the relative concentrations of the two gases. In the last experiment listed the oxygen concentration was very high and the result is somewhat uncertain since the rate gradually decreased with time; quite large quantities of yellow mercuric oxide were formed in the cell and in the tube leading to the scrubbing bottle, which seriously interfered with rate measurements in the later stages of the experiment. In most of the experiments to be described practically no mercuric oxide deposited in the reaction chamber and only small quantities in the tube leading to the absorber. After each experiment, however, the system was washed out with nitric acid and water to remove any oxide formed.

In all the ensuing experiments the reaction was carried on for a sufficient period to ensure a reliable value for the rate. The fourth column gives a measure of the total amount of reaction, from which the duration of the

experiment can be calculated. The fifth column gives the total amount of peroxide formed measured as cc. of gas at 0° and 760 mm. pressure. When the ratio (cc. H₂O₂)/(total pressure change in mm.) falls below 1.10, it indicates that in the later stages of the reaction some of the peroxide initially formed was being decomposed; this always showed in the experiments as a decrease in rate. A value of the ratio of 1.10 corresponds to pure peroxide as the reaction product. The value of the data in these two columns is to indicate the extent to which it is possible to avoid decomposition of the peroxide.

TABLE II

DATA WITH VARYING CONCENTRATIONS OF THE TWO GASES

Gas saturated with mercury vapor at 50°; temperature of reaction chamber, 60°; temperature of mercury in arc, 30°; arc current, 15 amps.

p_{H_2} , mm.	p_{O_2} , mm.	Rate in mm./min	Total press. change	Cc. of H ₂ O ₂ formed	N_{H_2}	Rate/ N_{H_2}
581	237	17 22	443	408	0.79	24.7
740	130	20	236	212	.92	21.7
425	368	12 3	597	326	.58	21.2
146	699	3	106	43	.155	19.9

In Table III the results are given for another series of experiments with an arc current of 1 ampere.

TABLE III

RESULTS WITH ARC CURRENT OF 1 AMPERE

Gas saturated with mercury vapor at 40°; temperature of reaction chamber, 60°; temperature of mercury in arc, 40°; arc current, 1 amp.

p_{H_2} , mm.	p_{O_2} , mm.	Rate in mm./min	Total press. change	Cc. of H ₂ O ₂ formed	N_{H_2}	Rate/ N_{H_2}
581	239	1 52	148	146	0.71	2.14
775	58	2 00			0.93	2.15
781	10	2 1			0.99	2.12
364	475	0 92			0.43	2.14

The constancy of the reaction velocity constants given in the last column of Tables II and III shows that in these experiments the rate of hydrogen peroxide formation is proportional to the mole fraction of hydrogen present.

$$\frac{d}{dt} (H_2O_2) = K \frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$

In the previous investigation¹ using the static system, this same equation was found to hold for the rate of water formation, which seems to indicate that in the previous experiments the rate of decomposition of hydrogen peroxide was of the same order of magnitude as its rate of formation. One of the interesting features of this work is the removal of practically all of the hydrogen peroxide undecomposed.

Variation of Rate with Mercury Concentration

An attempt was next made to study the effect of the various other controllable variables on the rate of the reaction. It was possible to vary the

mercury vapor concentration over a twenty-five fold range and the results obtained are listed in Tables IV and V.

TABLE IV

RESULTS WITH VARIABLE MERCURY VAPOR CONCENTRATION

Temperature of reaction chamber, 65°; temperature of mercury in arc, 30°; arc current, 15–15.5 amps.; p_{H_2} , 580 mm.; p_{O_2} , 250 mm.

Temp. of Hg, saturator, °C.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed	p_{H_2} in mm.
19	6.3	436	467	0.0013
31	11.8	414	463	
41	16.0	434	449	.006
50	17–22	443	407	
61	18.6	476	417	.03

A later series of experiments with different operating conditions is given in Table V.

TABLE V

LATER RESULTS WITH VARIABLE MERCURY VAPOR CONCENTRATION

Temperature of reaction chamber, 95°; temperature of mercury in arc, 41°; arc current, 3 amps.

Temp. of Hg saturator, °C.	Rate in mm./min.	Total press. change	Cc. of H_2O_2 formed
19	2.93	293	329
31	5.20	391	421
64	5.47	330	250

It was observed that quite large quantities of mercuric oxide were formed in the experiments with high mercury concentrations and the yield of hydrogen peroxide for a given pressure change was much lower, pointing to a considerable amount of decomposition.

Variation of Rate with Mercury Pressure in Arc

A number of experiments were performed varying the temperature of the mercury in the arc and the results are given in Tables VI and VII.

TABLE VI

RESULTS WITH VARIABLE MERCURY ARC TEMPERATURE

Temperature of reaction chamber, 69°; temperature of mercury saturator, 50°; arc current, 3.1 amps.; p_{H_2} , 580 mm.; p_{O_2} , 250 mm.

Temp. of Hg in arc, °C.	17	40	51	87
Rate in mm./min.	2.5	7.5	7.0	2.0

This was all one experiment; the total pressure change was 443 mm. and 417 cc. of H_2O_2 was formed. The next experiment was made without removing any mercuric oxide formed in the previous one.

Temp. of Hg in arc, °C.	40	11	32	40	52
Rate in mm./min.	6.0	2.2	5.6	6.1	5.7

Total pressure change, 502 mm.; cc. of H_2O_2 formed, 293.

It will be observed that in the experiment with the dirty cell the amount of peroxide decomposed was quite large. It may well be that mercuric oxide plays an important role in this decomposition. In Table VII is listed later series of experiments which were performed under better controlled conditions.

TABLE VII

LATER EXPERIMENTS WITH VARIABLE MERCURY ARC TEMPERATURE

Temperature of mercury saturator, 31°; temperature of reaction chamber, 95°; arc current, 3 amps.

Temp. of Hg in arc, °C.	Rate of mm./min.	Total press. change	Cc. of H ₂ O ₂ formed
13	1.40	199	218
29	3.22	221	246
41	5.20	391	420
49	4.66	396	444
61	3.17	403	469
81	1.76	275	326

This indicates that under these conditions the optimum concentration of mercury vapor for securing the largest amount of resonance light is about 0.01 mm.

Variation of Rate with Arc Current

In the next series of experiments the arc current was varied over as wide limits as possible.

TABLE VIII

RESULTS WITH WIDELY VARIED ARC CURRENT

Temperature of mercury in arc, 52°; temperature of mercury saturator, 50°; temperature of reaction chamber, 70°; p_{H_2} , 580 mm.; p_{O_2} , 250 mm.

Arc current	25	15	10
Rate	18.2	13.3	12.3

Total pressure change, 464 mm.; cc. of H₂O₂ formed, 327.

The data given in this table were collected in a single experiment and are not so reliable as those in the following table but are included to give a complete record of all the experiments carried out.

TABLE IX

RESULTS WITH WIDELY VARIED ARC CURRENT

Temperature of Hg in arc, 42°; temperature of mercury saturator, 31°; temperature of reaction chamber, 95°.

Arc current	Rate	Total press. change	Cc. of H ₂ O ₂ formed
15.5	14.9	337	331
21	20.9	360	371
9.7	11.0	366	395
5	7.75		
3	5.20	391	422

All the data obtained on the variation of rate with arc current are plotted in Fig. 2. It will be observed that in this graph the rate is proportional to

the current up to 6 amps. and then commences to diverge from strict proportionality so that at 21 amps. the rate has fallen to two-thirds of that calculated from the 6 amp. rate. It is quite probable that the amount of resonance radiation given by the arc varies in a similar manner with the current, in which case the reaction rate would be proportional to the first power of the light intensity. Measurements are now in progress to check up quantitatively on this part of the problem.

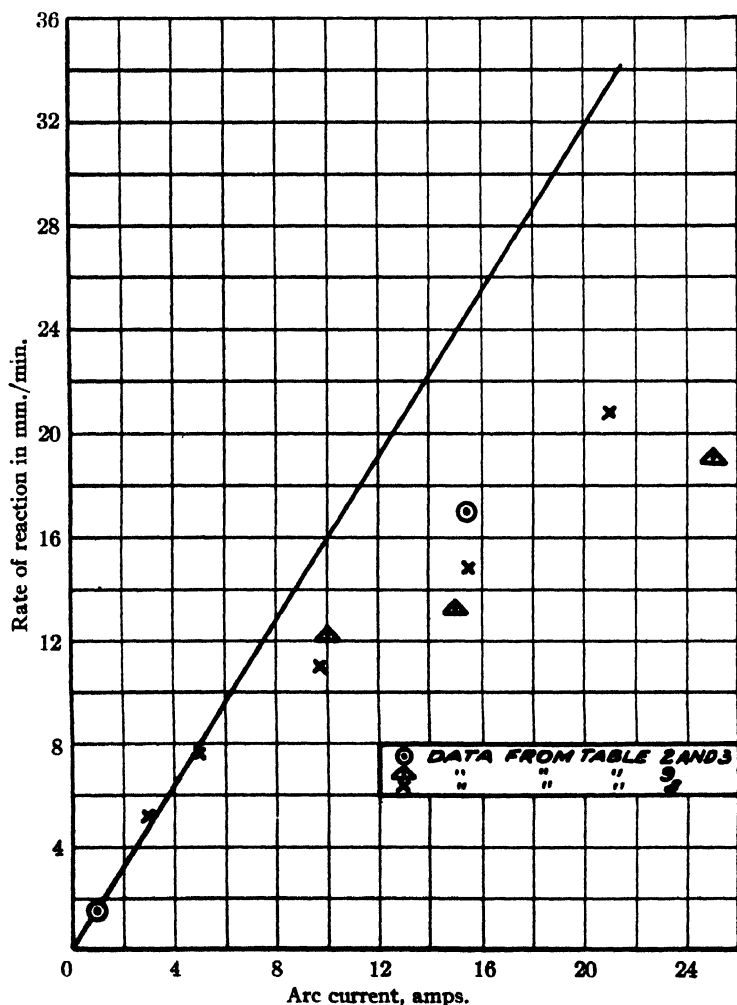


Fig. 2.

True Temperature Coefficient of Reaction

In the first half of this investigation very little difficulty was experienced in obtaining reproducible results, but towards the end it became more

difficult and the source of the difficulty was never definitely located. For this reason, the experiments on the temperature coefficient are not as reliable as those given above. They are, however, the average results of a large number of experiments and give the temperature coefficient within a factor of a few per cent. In Table X we have the result of a single experiment while Table XI is the average of a large series.

TABLE X
RESULTS OF ONE EXPERIMENT

Temperature of mercury saturator, 30°; temperature of mercury in arc, 40°; arc current, 3 amps.; p_{H_2} , 598 mm.; p_{O_2} , 241 mm.

Temperature of reaction chamber, °C.	Rate in mm./min.	N_{H_2} (average)
96	4.56	0.735
40	3.08	0.783

When these results are calculated for the same mole fraction of hydrogen the temperature coefficient for a 10° rise in temperature comes out as 1.13.

TABLE XI
AVERAGES OF RESULTS

Temperature of mercury saturator, 32°; temperature of mercury in arc, 50°; p_{H_2} , 600 mm.; p_{O_2} , 260 mm.

Temperature of reaction chamber, °C.	Rate in mm./min.	Temperature of reaction chamber, °C.	Rate in mm./min.	
<i>Arc current 15 amps.</i>		<i>Arc current, 5 amps.</i>		
100	12.3	100	4.32	T. C. = 1.044
100	10.6	40	3.3	
100	11.8	100	3.80	
50	9.9	40	3.09	T. C. = 1.038
50	8.8			
100	10.5			
50	9.6			
<i>Averages</i>				
100	11.3			
50	9.4			

From this last series of measurements, it appears that the temperature coefficient is about 1.04. This is the order of magnitude usually found for a true photochemical reaction and if correct seems to indicate that the amount of energy absorbed by the system from the arc is independent of temperature.

Summary

1. The kinetics of the photochemical reaction between hydrogen and oxygen when sensitized by mercury vapor is given by the equation

$$\frac{d}{dt} (H_2O_2) = K \frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$

2. The optimum concentration of mercury vapor for the reaction is about 0.005 mm.; while higher concentrations give a greater rate of re-

action, this is offset by decomposition of the hydrogen peroxide initially formed.

3. The mercury vapor lamp gives the most resonance radiation (λ 2536.7 Å.) with a mercury pressure of about 0.01 mm.

4. The rate of reaction is roughly proportional to the arc current, suggesting that the rate varies as the first power of the light intensity.

5. The temperature coefficient of the reaction is 1.04.

6. The product of reaction is predominantly hydrogen peroxide, the maximum rate of formation observed being two grams per hour.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SYSTEM $\text{MgSO}_4\text{-H}_2\text{O}$ FROM 68 TO 240°¹

BY HOMER LOUIS ROBSON

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Five hydrates of magnesium sulfate may exist in contact with aqueous solutions of the salt near their boiling points. These are the monoclinic or ordinary hexahydrate, the penta-, tetra-, five-fourths and monohydrates.² Of these, the hexahydrate is the stable phase from 48.4° to 68° and may be followed up to 100°. The transition point of the hexahydrate to the monohydrate was found by Van't Hoff, Meyerhoffer and Smith⁴ to be 68°, and the monohydrate is the stable phase from this temperature up to 240°. They also found the transition of the hexahydrate into the five-fourths hydrate to lie between 68 and 72°⁶ and that of the pentahydrate into the tetrahydrate to lie close to 77.5°. The transition

¹ Part of a thesis submitted to the Faculty of the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Other hydrates of magnesium sulfate are the dodecahydrate prepared by Fritsche (a) (Fritsche, *Pogg. Ann.*, **42**, 577 (1842), see also observations by F. G. Cottrell, mentioned by Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1035), the rhombic heptahydrate or epsom salt (b) (for properties see E. S. Larsen, "The Microscopic Identification of the Non-Opaque Minerals," Bulletin 679, U. S. Geol. Survey, 1921, and Groth, "Chemische Krystallographie," Part 2, **1908**, p. 429), the tetragonal hexahydrate prepared by L. de Boisbaudran (c) (de Boisbaudran, *Ann. chim. phys.*, (4) **18**, 260 (1869)), the monoclinic heptahydrate prepared by Loewel (d) (Loewel, *Ann. chim. phys.*, (3) **43**, 405 (1855); Groth, ref. 2 b, p. 431), and the dihydrate.

³ Carpenter and Jette, *THIS JOURNAL*, **45**, 578 (1923). The rhombic heptahydrate is the stable phase below this temperature.

⁴ Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1034.

⁵ The nearness of this point to that found for the hexahydrate—monohydrate transition caused them to doubt the identity of the five-fourths hydrate (ref. 4, footnote to page 1037).

point of the hexahydrate into the pentahydrate was found by T. Estreicher-Rozbiersky to be 77.5° .^{4,6}

The transition of the tetrahydrate into the hexahydrate occurs fairly rapidly. A mixture of the tetrahydrate and a solution saturated with respect to it was cooled one degree per hour while being stirred; at 77° lumps which were found to contain the hexahydrate formed in the mixture. The hexahydrate may form alone if the solution is slowly evaporated at its boiling point. If the evaporation is rapid, or if the solution is agitated, the penta- and tetrahydrates form along with the hexahydrate. The tetrahydrate is the more stable of the three and solutions in equilibrium with it may be stirred for several days at 100° without the formation of lower hydrates. The five-fourths, and possibly the monohydrate also, may be induced to form by violent boiling or by inoculation from crusts formed on the sides of the vessel during evaporation. The solution comes to equilibrium with these slowly.

Preparation of Hydrates

Crystals of the penta- and tetrahydrates were first obtained by Wyruboff⁷ by evaporation of a solution of magnesium sulfate acidified with sulfuric acid at 50° . They have also been obtained by Van't Hoff and Estreicher-Rozbiersky⁸ by the evaporation of solutions of magnesium sulfate containing magnesium chloride at 25° . Playfair⁹ and Thorpe and Watts¹⁰ claimed to have prepared the pentahydrate by drying the heptahydrate to constant weight over sulfuric acid and, according to Millon,¹¹ the pentahydrate may be prepared by heating the heptahydrate to 40° in moist air.

Van't Hoff and Dawson¹² found that above 40° the tetrahydrate was replaced by the dihydrate when in contact with solutions of magnesium sulfate also saturated with respect to $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. This hydrate was unstable and at 65° was replaced by the five-fourths hydrate, which apparently was the stable phase in these solutions down to 20° . Both the

⁴ Wiedemann, *Pogg. Ann.*, 17, 571 (1882), from dilatometric observations, concluded that there were two forms of the hexahydrate with a transition point under 92° . To test this, solutions in equilibrium with the monoclinic hexahydrate at 95° and containing a very little of the solid in suspension were inoculated with crystals of tetragonal nickel sulfate hexahydrate, which L. de Boisbaudran²⁰ had found to be isomorphous with tetragonal magnesium sulfate hexahydrate. This did not cause the formation of a tetragonal (optically uniaxial) hydrate of magnesium sulfate, so that it does not seem probable that the tetragonal hexahydrate is formed at this temperature. No other hexahydrate of magnesium sulfate is known. Van't Hoff, Meyerhoffer and Smith⁴ suggest that he observed the change of the pentahydrate to the tetrahydrate.

⁷ Wyruboff, *Bull. soc. franç. minéral.*, 12, 75, 366 (1889).

⁸ Van't Hoff and Estreicher-Rozbiersky, *Sitzb. preuss. Akad. Wiss.*, 1898, 487.

⁹ Described by Thorpe and Watts, *Ref.* 10.

¹⁰ Thorpe and Watts, *J. Chem. Soc.*, 37, 102 (1880).

¹¹ Millon, *Ann. chim. phys.*, (3) 13, 134 (1845).

¹² Van't Hoff and Dawson, *Sitzb. preuss. Akad. Wiss.*, 1899, 340.

dihydrate and the five-fourths hydrate are unstable with respect to the monohydrate above about 25° ¹³ in contact with solid $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, but the monohydrate ordinarily does not form spontaneously under 75 – 85° .

Playfair,⁹ Hannay¹⁴ and Millon¹⁵ observed that the dihydrate was formed on drying the heptahydrate in air at 100° . Hannay stated that his data favored the existence of a trihydrate but an examination of his curves does not warrant this. Millon obtained evidence in favor of a hydrate intermediate between the di- and monohydrates at 115° and this was confirmed by Van't Hoff and Dawson,¹² who found that the rate of water loss drops to one-tenth after the composition $\text{MgSO}_4 \cdot 5/4\text{H}_2\text{O}$ has been reached. The dihydrate is best prepared in this way by allowing crystals of the heptahydrate to effloresce in air at 50 – 60° and then heating the powder at 100° for two hours. The product was found to contain crystals of the tetrahydrate and some monohydrate as a very fine powder. After drying in an oven at 95° for one day, the moisture content of a 3 mm. layer of the salt was found to be 17.5%, after two days, 15.6% and after three days 14.4%, showing a slowing up at the composition of the five-fourths hydrate, which has 15.7% of water. The dehydration can be continued to the monohydrate at this temperature. If the crystals of the heptahydrate are allowed to melt and then dried at 100° , a cake is formed containing the monohydrate.

Playfair⁹ prepared the dihydrate by the action of boiling absolute alcohol on the heptahydrate. This is not a satisfactory method for the preparation of this salt. The heptahydrate is rapidly converted into the tetrahydrate by this treatment. If the tetrahydrate is boiled with three to four times its weight of absolute alcohol for twelve hours, most of it is converted into the dihydrate, but considerable five-fourths hydrate and finely divided monohydrate are formed with it. On further boiling the dihydrate and five-fourths hydrate may be converted into the monohydrate.

The monohydrate occurs in nature and is called kieserite. It may be prepared by heating the higher hydrates to 140 – 180° for several days.^{9,10} Kieserite loses its water slowly at 250° and rapidly at 350° . Water may be determined readily by heating to 500° in an open crucible. The decomposition of anhydrous magnesium sulfate was found to be inappreciable at 750° but rapid above 850° .¹⁶

¹³ Van't Hoff and Meyerhoffer, *Sitzb. preuss. Akad. Wiss.*, 1904, 1418, inferred that the monohydrate was formed in contact with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ above 18° but did not actually determine the transition point. Their conclusion was not confirmed by W. C. Blasdale, *J. Ind. Eng. Chem.*, 12, 164 (1920), who found that the monohydrate was apparently unstable at 25° .

¹⁴ Hannay, *J. Chem. Soc.*, (2) 32, 381 (1877).

¹⁵ Millon, ref. 11. He also states that the dihydrate may be prepared by keeping the heptahydrate in contact with very dry air at 35° for one month. The product probably contains considerable monohydrate.

¹⁶ Cf. Marchali, *J. chim. phys.*, 22, 325 (1925).

Solubility Relations

A search was made for the solubility curve of the dihydrate between 70° and the boiling point, but it was not found. Solutions in equilibrium with the hexahydrate or tetrahydrate slowly came to equilibrium with the monohydrate when inoculated with preparations of the dihydrate, most of which had close to the theoretical water content, but contained some monohydrate.

The curve of the five-fourths hydrate was not determined, but from similar experiments it would appear to lie very slightly above the curve for the monohydrate at 95°.

Wyruboff¹⁷ observed that the solubility curves of the penta- and tetrahydrates were close together in sulfuric acid solutions at 50°. They are

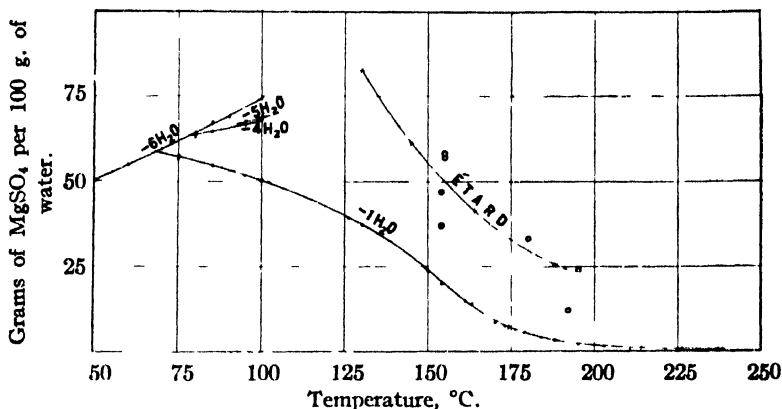


Fig. 1.—The system $\text{MgSO}_4\text{-H}_2\text{O}$ from 68 to 240°.

apparently close together in aqueous solutions at 100°. Both hydrates are formed in the boiling solution but on stirring at 95° the pentahydrate slowly disappears and the solubility drops slightly, from which it is assumed that the pentahydrate curve lies slightly above that of the tetrahydrate, as indicated in Fig. 1.

Geiger¹⁸ gave for the solubility at 83°, 67.2 g. of MgSO_4 per 100 g. of water, but the solid phase present with his solutions was probably the hexahydrate. Smith¹⁸ gave the concentration of a solution in equilibrium with kieserite at 80° as 62.8 g. of MgSO_4 per 100 g. of water and Meyerhoffer¹⁸ obtained 68.5 at 99.4°. These points fall on the tetrahydrate curve as determined in this investigation, so that the solid phase was probably the tetrahydrate and not kieserite. Mayeda¹⁹ gave 51.2 g. per 100 g. of water at 105°, a value slightly above the curve for the mono-

¹⁷ Ref. 7, p. 369.

¹⁸ From Landolt-Bornstein Tabellen, 1923 ed.

¹⁹ Mayeda, *J. Chem. Ind. (Japan)*, 23, 573 (1920).

hydrate given in this paper. Étard²⁰ gave for the solubility of magnesium sulfate the following values.

Temperature, °C.	130	145	164	188
Per cent. MgSO ₄ , liquid phase	45.3	38.0	29.3	20.4
G. of MgSO ₄ per 100 g. of water (calcd.)	82.8	61.3	41.4	25.6

Étard enclosed his solutions in sealed tubes divided into two equal chambers by a constriction in the middle. The salt and solution were placed in one chamber and the tube was sealed off; the tube was then placed in a thermostat and after shaking a few times the liquid phase was poured into the empty chamber through the constriction, which acted as a filter. The tube was then cooled and the contents analyzed. He does not state the time given for the solutions to come to equilibrium. Suspensions of kieserite in solutions in equilibrium with it require several hours or even days to settle and Étard's liquid phase probably contained some finely divided kieserite. The salt may be more granular when formed from a supersaturated solution with comparatively little agitation.

Étard's results may give the composition of solutions on the supersolubility curve of kieserite. On this assumption, solutions lying below the curve could be agitated without depositing the salt, while those above it would deposit kieserite by spontaneous crystallization upon agitation.²¹

The data given in the following table are in agreement with this interpretation of Étard's data.

TABLE I

Temp., °C.	Hours stirred	Liquid phase ^a Before stirring	After stirring	Salt formed	Remarks
154	4	37	same	none	below Étard's curve
154	1½	47	same	none	below Étard's curve
192	1	12	same	none	below Étard's curve
155	1½	57	37	kieserite	above Étard's curve
155	1½	58	32	kieserite	above Étard's curve
195	3	24	4.6	kieserite	above Étard's curve

^a Liquid phase given in g. of MgSO₄ per 100 g. of water.

The trials in this table were not inoculated with kieserite. They are represented by circles in Fig. 1, while Étard's measurements are represented by crosses. Étard observed that a solution containing 33.3 g. of magnesium sulfate per 100 g. of water crystallized spontaneously at 180°.

When a solution exceeds the supersolubility curve, crystallization occurs spontaneously upon agitation, with the formation of many very small crystals. As the crystal surface exposed by these very fine crystals is large, the formation of a small quantity of them would be expected to be

²⁰ Étard, *Ann. chim. phys.*, (7) 2, 503 (1894).

²¹ Blasdale, "Equilibria in Saturated Salt Solutions," A. C. S. Monograph Series, No. 31, 1927, p. 66.

more effective in reducing the supersaturation of the solution than the presence of several times as much of the salt in a coarser crystalline form. Trials which became inoculated through exceeding the supersolubility curve came to equilibrium more rapidly than those which were inoculated with 5 or 10% of kieserite by weight.

The solubility curve of kieserite is given by Landolt-Börnstein, 1923 ed., as passing through the values given by Smith and Meyerhoffer and the last two values given by Étard.

Identification of Hydrates

The hydrates of magnesium sulfate occurring near the boiling point may be identified with the aid of the petrographic microscope. After a portion of the liquid phase had been taken for analysis, the suspended hydrates were allowed to settle for a few minutes and a small quantity was removed with a glass or perforated platinum spoon. When the hexahydrate, pentahydrate or tetrahydrate was present, this was rubbed dry on warmed filter paper or pressed on a porous plate warmed to 80°. These hydrates are partially decomposed by pressing dry on a porous plate warmed to 100°, which treatment was required to dry the monohydrate. Some hexahydrate formed by cooling of the adhering liquor while pressing the solids dry between filter paper. The absorbent cotton rolls used by dentists were found of value in drying the samples. Some of the samples were washed with alcohol, but this is objectionable as the addition of absolute alcohol to a saturated solution of magnesium sulfate at 80–90° usually precipitates some tetrahydrate.

The optical properties of the hydrates are given in the following table.²²

TABLE II

THE OPTICAL PROPERTIES OF THE HYDRATES

Hydrate	α	β	γ	2V sign disp.	Orientation	System
Hexa-	1.438	1.463	1.465	29° - $\rho > v$	$Y = b, X \wedge c - 25^\circ$	Monoclinic
Penta-	1.482	1.492	1.493	45° - $\rho < v$	X near b	Triclinic
Tetra-	1.490	1.491	1.497	50° + $\rho > v$	$Z = b, X \wedge c 81^\circ$	Monoclinic
Di-		1.493	radiate clusters of very fine needles			
Five-fourths	1.512	1.530	indices of diamond-shaped crystals			
Mono-	1.523	1.535	1.586	57° + $\rho > v$	$Y = b, Z \wedge c 76\frac{1}{2}^\circ$	Monoclinic

The monoclinic hexahydrate may be recognized by its indices of refraction and small optic angle. The penta- and tetrahydrates may be distinguished by their difference in sign. When prepared from solutions containing magnesium chloride, the tetrahydrate appears in six-sided

²² The nomenclature is that employed by Larsen, ref. 2 b. The optical orientation of the hexa-, penta- and tetrahydrates, with their optic angles and dispersion, is given by Wyrouboff, ref. 7. The indices of refraction given in this table are probably accurate to ± 0.003 . The optical properties of the monohydrate are given by Larsen, ref. 2 b, p. 211.

plates, showing the forms $m(110)$ and $b(010)$.²³ The angle $m \wedge m$ is $48^\circ 40'$ and frequently this angle may be measured to within 1° under the microscope. No dome or pyramid faces were observed. Cleavage was observed parallel to $a(100)$ and $b(010)$. The pentahydrate and hexahydrate are elongated in the direction of the c axis, and do not show cleavage. Crushed fragments of the three hydrates look very similar when placed between crossed nicols with parallel light.

The needles of the dihydrate show varying extinction angles and elongation and were too fine for the observation of their optical properties. Single crystals of the five-fourths hydrate were not observed. The

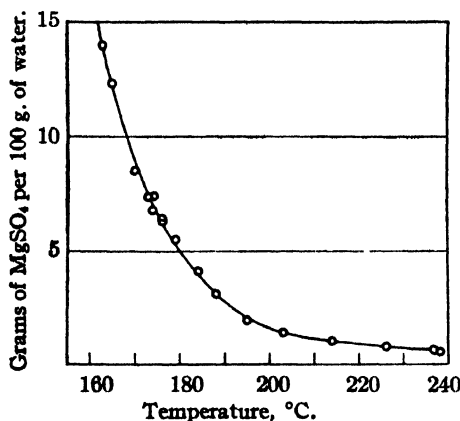


Fig. 2.—The system $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ from 160 to 240° .

diamond-shaped crystals show crossed twinning, with the opposite quadrants extinguishing at 5° to the symmetry plane of the diamond. The twinning is often imperfect.

In all the trials except those above 200° kieserite occurred in aggregates of very small grains, which were too small for the observation of crystal structure or optical character. It may be recognized by its high index of refraction and fine-grained structure. Solutions inoculated with preparations of kieserite and al-

lowed to come to equilibrium with it had minimum contents of magnesium sulfate. After trials at 226° , 240° and 246° had been sampled, the valve of the solubility bomb (see below) was left open until all of the liquid phase had passed out. The bomb was then quickly opened and the solid phase found to be granular and quite dry. On analysis it gave 1.00, 0.99 and 0.98 molecules of water per molecule of magnesium sulfate, respectively. Some of the grains were large enough so that interference figures could be obtained. As there is no break in the solubility curve, this was taken as evidence that the solid phase present in the trials between 100° and 240° and which fell on the "monohydrate" curve was in reality the monohydrate.

Description of Apparatus

In the experiments under 100° , the solutions in contact with the solid phase were stirred in 4×30 cm. tubes immersed in an oil-bath kept constant to within half a degree. The tube was closed off with a rubber stopper where it projected above the level of the

²³ Indices assigned by Groth, ref. 2 b, p. 413.

oil, the stirring screw coming through a glass tubing which passed through this stopper. After sufficient stirring, about 30 g. of the solution was filtered through a dried alundum thimble²⁴ into a weight pipet and analyzed.

The trials above 100° were made with a gold-plated bomb of Monel metal, shown in Fig. 3. This consisted of a cylindrical vessel A, 9 cm. long by 3.25 cm. inside diameter, and a head-piece B which carried the filtering apparatus and the needle valve. The upper part of the cylinder was 4 cm. in diameter and was threaded to receive the head, which screwed into it against a flat gold washer C resting on a 3mm. shoulder. The gold washer was $\frac{1}{60}$ inch thick and the volume of the cylinder up to the shoulder was 70 cc. This arrangement gave a joint that was satisfactory for the pressures encountered up to 240° but which did not hold well at higher temperatures.

The head was hollowed out to a depth of 1 cm. to give a flat surface 3.5 cm. in diameter, and the filtering apparatus was mounted in this recession. This consisted of an alundum disk D, $1 \times \frac{1}{8}$ inche, with a beveled edge, the composition being given by the Norton Co. as RA98. This was held against the flat surface of the head by four prongs attached to an expansion ring E. Under the alundum disk was an asbestos pad, then a flat gold washer F which was 3 cm. in diameter and $\frac{1}{100}$ inch thick, with a 6mm. hole in the center. Under this washer was another asbestos pad. The asbestos pads were prepared by suspending carefully selected, long fiber asbestos in water and then slowly evaporating off the water. They could be compressed to a thickness of $\frac{1}{600}$ of an inch.

The hole in the washer gave an empty space of negligible volume directly over the needle valve G. After the salt and water mixture had been stirred the required length of time, the bomb was removed from the bath and clamped head downwards. When the needle valve was opened, the liquid phase was forced through the alundum disk into the valve chamber under its own vapor pressure and through

an opening in the side of this chamber into the delivery tube J. The delivery tube was a short piece of $\frac{1}{8}$ -inch copper tubing attached to a brass piece which screwed into the opening in the head. While the bomb was in the oil-bath, the opening was closed with a plug H. The delivery tube was connected to the condenser, which was a U-shaped copper tube $\frac{3}{4}$ inch in diameter and two feet long, weighing 125 g. During sampling this was partially immersed in ice water. The end not connected to the delivery tube was open to the atmosphere. No water vapor was observed to come out of this end.

After about 30 g. of liquid had been drawn off, the valve was closed and the contents of the condenser analyzed. With trials run above 160° this quantity of liquid was obtained in about thirty seconds, depending upon the amount of solid salt inside the

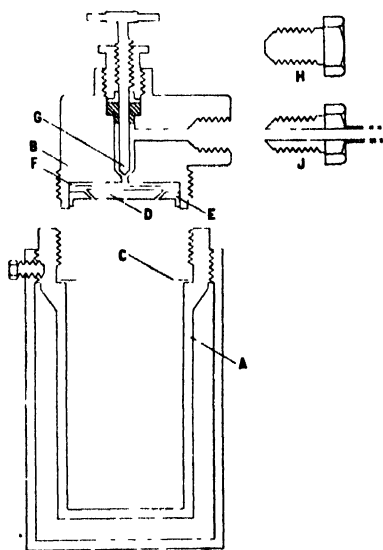


Fig. 3.—Solubility bomb.

²⁴ The thimbles were supplied by the Norton Company. Those most satisfactory were of mix RA98. The solutions filtered through thimbles of this composition rapidly, carrying a negligible quantity of kieserite into the sample where it was present in the tubes. Thimbles of composition RA225 gave clear solutions, but the liquid phase passed through them very slowly.

bomb. At lower temperatures a longer time was required, the trial at 126° taking two and one-half minutes. The time taken for the liquid phase to pass the filter did not seem to affect the results.

The bomb had an outer brass shell to prevent rapid loss of heat after it had been taken from the bath. After charging, the bomb was fastened to a stirring device and rotated at 60 r.p.m. in a bath of meprolene kept at constant temperature within half a degree. The bath was thoroughly stirred and the temperature taken with two calibrated thermometers. When stirred a sufficient length of time, the bomb was taken from the bath, clamped to a stand, the delivery tube and condenser were attached and the valve was opened, this taking about one minute. From preliminary experiments with ice it was estimated that the contents of the bomb were within one degree of the temperature of the bath after twenty-five minutes of stirring.

This apparatus was designed to measure equilibrium in ternary salt-water systems, but with most of the salt solutions experimented with crystals formed in the valve chamber during sampling. With magnesium sulfate, the negative slope of the solubility curve with temperature, and its tendency to supersaturate, prevented error from this source.

An attempt was made to employ a filter outside the bomb. This consisted of a male brass piece which screwed into the opening in the head of the bomb, and also into a 1" brass sleeve, which was closed at one end except for an eighth-inch delivery tube going to the condenser as in other experiments. An alundum disk was placed between two lead washers in the sleeve and the male piece screwed tightly against the outer washer. On opening the valve, the liquid was forced out through the valve chamber and the alundum disc into the discharge tube and so to the condenser.

This arrangement was unsatisfactory, chiefly because the liquid phase cooled after passing through the needle valve, due to the release of pressure and consequent evaporation, and so was filtered from any solid salt it carried along with it at a lower temperature than it had before leaving the bomb. With kieserite the solubility increased with falling temperature and this apparatus gave high results. As there is a drop in pressure across the filter, any filter which the liquid phase might pass after leaving the needle valve would become cooled by the evaporation of some of the water and so introduce an error. To avoid this the filter must be placed inside the bomb.

Results

Solutions came to equilibrium with the hexahydrate in a few minutes, and to equilibrium with the penta- and tetrahydrates fairly rapidly. Three to seven days were required for solutions to come to equilibrium with kieserite under 100° , unless an abundance of solid phase was present. Equilibrium was not obtained in less than twenty-four hours' stirring under 160° nor with less than four hours' stirring under 190° , but was obtained after stirring for one-half hour at 238° . Many trials, well inoculated, which were stirred for shorter periods gave high results.

There appears to be a relation between the degree of crystallographic perfection exhibited by a salt and the rapidity with which it comes to equilibrium with its aqueous solution. Thus kieserite is poorly crystallized under 200° and comes to equilibrium slowly. Above this temperature it is granular and comes to equilibrium rapidly. The dihydrate would be expected to come to equilibrium slowly. Salts such as sodium chloride, potassium chloride and potassium sulfate, which are well crystallized, formed crystals in the valve chamber in experiments at 150° even when no delivery tube was employed, while sodium sulfate and sodium carbonate, which are less well crystallized, could be filtered with the external filter, but the solutions altered in composition in passing through the apparatus.

The trials made with the bomb fall on a definite line, as may be seen from Fig. 2, in which the values from 160 to 240° are plotted on a larger scale. All the trials which fulfilled the requirements of adequate inoculation, duration of stirring and proper filtering fell within one degree of this curve. The samples were analyzed by precipitating an aliquot part with barium chloride, the method being accurate to 0.1% by trials against pure sodium sulfate.

Table III gives the results of experiments which are considered satisfactory. Three values of Mulder¹⁸ and those of Smith and Meyerhoffer previously mentioned are included. The values are plotted in Fig. 1.

TABLE III
COMPOSITION OF SOLUTIONS SATURATED WITH MgSO_4

Temp., °C.	Liquid phase, g. of MgSO_4 per 10 g. of water	Hours stirred	Remarks
70	59.4		By Mulder, hexahydrate
75	56.5	150	Kieserite
75	57.4	150	Kieserite
80	64.2		By Mulder, hexahydrate
80	62.8		By Smith
85	67.1	2	Hexahydrate
85	67.6	1 1/4	Hexahydrate
85	64.3	8	Penta- and tetrahydrates
85	64.6	5	Penta- and tetrahydrates
85	64.7	24	Penta- and tetrahydrates
85	64.1	24	Tetrahydrate
85	64.3	48	Tetrahydrate
85	54.75	150	Kieserite
85	54.75	150	Kieserite
85	55.05	150	Kieserite
90	69.0		By Mulder, hexahydrate
95	67.7	1	Penta- and tetrahydrates
95	67.2	4	Penta- and tetrahydrates
95	66.6	24	Tetrahydrate
95	66.2	30	Tetrahydrate
95	52.0	150	Kieserite

TABLE III (Concluded)

Temp., °C.	Liquid phase, g. of $MgSO_4$ per 10 g. of water	Hours stirred	Remarks
95	52.1	150	Kieserite
95	51.6	150	Kieserite
95	51.6	100	Kieserite
95	51.6	96	Kieserite
99.4	68.5		By Meyerhoffer
100	74.6	2 minutes after concentration by boiling	Hexahydrate
100	68.1	$\frac{1}{2}$	Penta- and tetrahydrates
100	67.7	$1\frac{1}{2}$	Penta- and tetrahydrates
100	50.4	40	Kieserite
126	39.3	96	Kieserite
130	37.2	65	Kieserite
150	23.9	24	Kieserite
154	19.8	48	Kieserite
161	14.8	24	Kieserite
163	14.0	24	Kieserite
165	12.3	12	Kieserite
170	8.5	18	Kieserite
173	7.4	24	Kieserite
174	7.4	48	Kieserite
174	6.8	24	Kieserite
176	6.3	5	Kieserite
176	6.4	18	Kieserite
179	5.5	5	Kieserite
184	4.1	12	Kieserite
188	3.1	4	Kieserite
195	1.9	18	Kieserite
203	1.4	36	Kieserite
214	1.05	34	Kieserite
226	.78	$1\frac{1}{2}$	Kieserite
237	.64	12	Kieserite
238	.56	$\frac{1}{2}$	Kieserite

In conclusion, the author wishes to express his thanks to Professor W. C. Blasdale for his valuable assistance during this research.

Summary

1. An apparatus has been described with which solubility determinations have been made up to 240° , with magnesium sulfate monohydrate as the solid phase.

2. The solubility curve of magnesium sulfate monohydrate was found to fall off rapidly with increase of temperature from 68 to 200° , and then to decrease slowly at least to 238° . Equilibrium was obtained very slowly under 200° and more rapidly above that temperature.

3. It has been suggested that the solubility measurements of Étard on this salt give the position of the supersolubility curve, and observations in agreement with this have been tabulated.

4. The solubility curves of magnesium sulfate hexa-, penta- and tetra-hydrate have been studied at 85, 95 and 100°.

5. The preparation of the hexa-, penta-, tetra-, di-, five-fourths and monohydrates of magnesium sulfate has been discussed, together with their identification with the aid of the petrographic microscope, and new optical data for the hexa-, penta, tetra-, di- and five-fourths hydrates have been given.

6. It has been suggested that there is a relation between the degree of crystallographic perfection exhibited by a salt and the rate at which it comes to equilibrium with its aqueous solution.

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THE CATALYTIC ACTIVITY AND ADSORPTIVE POWER OF SUPPORTED IRON, COBALT, NICKEL, COPPER AND SILVER

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This paper records the results of experiments on the activities of similarly prepared, supported iron, cobalt, nickel, copper and silver catalysts in the hydrogenation of ethylene. The experiments were undertaken with the view to determine the true relative activities of these metals as hydrogenation catalysts and to obtaining preliminary results on reaction kinetics.

The specific activity of a contact catalyst depends ultimately on its chemical nature. In addition, however, the catalytic effect as experimentally determined is conditioned by the area of surface exposed per unit volume of reactants and by its submicroscopic form, and these vary from one sample to the next. If a comparison of two substances as catalysts is desired, therefore, some standardization relative to surface characteristics is required. Bulk catalysts are out of the question, because the utmost care in preparation cannot ensure similarity of surface. Supported catalysts are of greater promise. The surface of a porous refractory will not change with any ordinary treatment and a film of the substance to be examined spread over the surface should assume the form of the latter. Consequently, if the catalysts to be compared are supported on average samples of the same refractory material, it may fairly be assumed that differences in activity are chiefly due to the specific properties of the substances under investigation.

We have prepared a uniform supply of crushed diatomite brick and have impregnated samples with such quantities of solutions of the nitrates of the metals as would correspond to 1 gram atom of metal per 1000 g. of dry brick. These samples were then dried slowly, calcined and reduced. The amount of the metal is admittedly arbitrary. It is approximately

that (10%) commonly used in preparing supported catalysts. We cannot say how thick a film it corresponds to, but we do know that the brick was not encrusted and appeared different only in color after treatment.

Preparation of Catalysts

The catalysts were all prepared in the same manner except for the final temperature of reduction. Non-Pareil porous, diatomite brick (kindly furnished by the Armstrong Cork Co.) was broken up and screened to 5-10 mesh. The granules were boiled in 15% nitric acid, washed repeatedly with distilled water and finally dried at a low red heat. Twenty g. (about 70 cc. apparent volume) was used for each catalyst. This was weighed out and placed in a small flask. It was found that such a sample would absorb nearly its own weight of water without becoming definitely wet. Solutions of the nitrates of the metals were accordingly made up to contain the requisite quantity of metal (corresponding to 1 gram atom per 1000 g. of brick) in 15 cc. of solution. This amount of solution was then placed in a dropping funnel and allowed to flow drop by drop onto the brick granules while the latter were agitated. The granules were then transferred to a section of large (2 inch) glass tubing and warm, dry air was slowly drawn over them. The tube was occasionally turned. The catalyst was then transferred to the catalyst bulb, which was sealed to the apparatus. The catalyst was then further heated gradually to 350-400° in a stream of air to calcine it and was finally reduced in hydrogen. Temperatures of reduction were: iron, 450°; cobalt, 370°; nickel, 300° (to 420° at end); copper, 200°; silver, 150° (to 250° at end). In no case was there evidence of a loss of metal from the support at any point in the procedure.

The nitrates were all c. p., those of cobalt and nickel being sold as nickel-free and cobalt-free, respectively.

The apparatus, method and preparation of gases were the same as those used in earlier work on this reaction.¹ The apparatus consisted of a catalyst bulb, manometer, gas buret, Töpler pump and gas reservoirs, all sealed together through suitable stop-cocks. Reaction rates were measured by the pressure decrease at constant volume. Adsorptions were obtained by comparing isotherms with that of helium.

Results

Our measurements are summarized in the following tables. Initial rates of reaction, obtained by extrapolation, are compared with initial partial pressures. Determinations were made at such temperatures as would give appreciable rates. In the case of nickel and cobalt, the rates were immeasurably high even at 20°, so that no quantitative data were obtained. Reaction was practically complete in the time (a few seconds) taken to admit the gases. We can only say that these substances are of another order of activity than any of the others.

The data on copper are taken from the work of Dr. C. A. Harris.²

The results indicate that supported iron and silver are considerably better catalysts and supported copper is a somewhat poorer catalyst than the average corresponding unsupported materials. Schmidt,³ for example, finds unsupported iron, prepared from the hydroxide, only moderately

¹ Pease, *This Journal*, 45, 1198 (1923).

² Pease and Harris, *ibid.*, 49, 2503 (1927).

³ Schmidt, *Z. physik. Chem.*, 118, 208 (1925).

TABLE I
REACTION RATES

Catalyst	Temp., °C.	Init. press., atm.		Init. rate, mm./min.
Iron	0	$\frac{1}{2}$	$\frac{1}{2}$	9.3
	0	$\frac{1}{3}$	$\frac{2}{3}$	6.9
	0	$\frac{2}{3}$	$\frac{1}{3}$	10.2
	0	$\frac{1}{2}$	$\frac{1}{2}$	7.5
	0	$\frac{1}{2}$	$\frac{1}{2}$	5.8
	10	$\frac{1}{2}$	$\frac{1}{2}$	9.0
	0	$\frac{1}{3}$	$\frac{1}{3}$	5.8
	20	$\frac{1}{2}$	$\frac{1}{2}$	12.7
	0	$\frac{1}{2}$	$\frac{1}{2}$	5.3
Copper	50	$\frac{1}{2}$	$\frac{1}{2}$	17.5
	50	$\frac{1}{3}$	$\frac{2}{3}$	11.8
	50	$\frac{2}{3}$	$\frac{1}{3}$	18.5
Silver	100	$\frac{1}{2}$	$\frac{1}{2}$	14.0
	100	$\frac{1}{3}$	$\frac{2}{3}$	9.7
	100	$\frac{2}{3}$	$\frac{1}{3}$	19.0
	50	$\frac{1}{2}$	$\frac{1}{2}$	1.8

TABLE II
ADSORPTIONS

Subs.	Gas	Temp. °C.	Temp., 10 mm.	Absorption, cc. 760 mm.
Nickel	H ₂	0	1.40	2.85
Cobalt	H ₂	0	0.50	1.28
Iron	H ₂	0	<0.05	0.10
Copper	H ₂	50	0.10	0.15
Silver	H ₂	100	<0.05	0.20
Nickel	C ₂ H ₄	0	0.95	9.00
Cobalt	C ₂ H ₄	0	0.80	8.20
Iron	C ₂ H ₄	0	1.95	12.70
Copper	C ₂ H ₄	50	0.20	3.05
Silver	C ₂ H ₄	100	0.10	1.15

active at 100°. Copper prepared from the carbonate is considerably more active than the iron, and silver has a very low and variable activity. Likewise Sabatier⁴ finds unsupported iron active only above 180°. The same is reported of copper but the authors have regularly employed copper in several forms at 0°. Silver is not even mentioned. Our supported iron catalyst is active at 0°, the copper at 50° and the silver at 100°.

We interpret these results to mean that the advantage of using a support is to lend stability where this is needed. The high temperatures (400–500°) required to reduce iron oxide promote deactivation by sintering, while the extreme softness of silver renders it especially susceptible in this regard. Copper, on the other hand, can be reduced at low temperatures and is only

⁴ Sabatier, Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York, 1923, p. 180.

moderately soft, so that a support is of no particular advantage. The fact that supported copper is actually less active than unsupported material is doubtless due to a smaller surface exposure. This is borne out by the uniformly low hydrogen adsorptions on all samples, even nickel adsorbing only 2.85 cc. at 1 atmosphere.

The adsorption of hydrogen by nickel and cobalt being considerably greater than by the other metals correlates with the high catalytic activity of the former. Adsorption of hydrogen by iron, copper and silver is small and probably the same within experimental error. Iron stands out with respect to ethylene adsorption and it is this apparently which places it above copper in catalytic activity.

As to reaction kinetics, the rate in the presence of silver at 100° is closely proportional to the hydrogen concentration and independent of the ethylene as was found for copper¹ at this temperature. Owing to the deactivation of the iron catalyst with use, the kinetics at 0° are not entirely clear. Excess of hydrogen undoubtedly increases the rate. The influence of ethylene is not great, but it is uncertain whether it is positive or negative. The kinetics in presence of copper are thoroughly treated in another paper.¹

The temperature coefficients give for the heats of activation, 6200 cal. in the case of iron between 0 and 20°, 13,200 cal. in the case of copper between 0 and 100°¹ and 9800 cal. in the case of silver between 50 and 100°.

These comparative results serve anew to emphasize the marked superiority of nickel and cobalt as hydrogenation catalysts over their neighbors, iron and copper, in the periodic table. Reference to Sabatier,⁴ reveals that the corresponding members of the two succeeding long periods stand in like relation. Thus, palladium and rhodium are considerably more active than ruthenium and silver and the same holds for platinum and presumably iridium, as compared with osmium and gold.

It is probably not without significance in catalytic theory that these highly active metals are those whose ions in solution enter into so great a variety of stable complexes. The tendency to form the latter seems to be traceable to electron sharing. Schmidt⁵ would have it that the function of the metal in catalytic hydrogenation is to provide a medium wherein hydrogen may become ionized. Without accepting in full the somewhat elaborate analysis of this investigator, one can readily agree that the electron systems of hydrogen and the substance hydrogenated are profoundly disturbed when they come in contact with the metal. It would be difficult to show that complete ionization actually takes place. The important point is, perhaps, that the associative property of the metal brings the reactants together, and the metal, by its tendency to share electrons, renders both labile, whereupon they may settle down into a system characterized by lower free energy.

¹ Ref. 3, p. 193.

Summary

1. Supported catalysts of iron, cobalt, nickel, copper and silver have been prepared by as nearly similar methods as possible and their activity in the hydrogenation of ethylene has been determined. Cobalt and nickel caused instantaneous action at -20° , iron was moderately active at 0° , copper at 50° and silver at 100° . The effect of the support appears to be to increase the effectiveness of all but copper. This is discussed.

2. Adsorption measurements show much more hydrogen adsorbed by nickel and cobalt than by the other metals, and more ethylene is adsorbed by iron.

3. Reaction kinetics in the presence of silver at 100° show that the rate is proportional to the hydrogen and independent of the ethylene concentration, as was found for copper. In the presence of iron at 0° , excess of hydrogen increases the rate while excess of ethylene exerts little influence.

4. Attention is called to the periodicity among the metals in catalytic properties and the correlation with complex ion formation. An association rather than a dissociation theory of catalytic hydrogenation is indicated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A SIMPLE TYPE OF FLOWING JUNCTION

BY E. J. ROBERTS AND F. FENWICK

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In connection with a study of the relation of the potential of an antimony electrode in contact with a solution saturated with antimony trioxide to the acidity of that solution, the problem of obtaining a reproducible liquid junction potential between the antimony electrode and the reference electrode (Ag, AgCl, 3.5 *M* KCl) became of prime importance. The electrode vessels used were modifications of the type described by Brönsted,¹ in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, to the junction; therefore, a flowing junction device requiring only small volumes of electrolyte and possessing an easy flexibility of adjustment to solutions of widely varying density was highly desirable. None of the arrangements previously described² meet these requirements. It was found, however, that by interposition of a thin mica plate vertically between the ends of the pair of horizontal exit tubes from the electrodes so that the streaming electrolytes flow slowly down opposite faces of the plate past a small hole, through which alone the solutions make contact, the resulting junction is satisfactory in all respects.

¹ Brönsted, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, 3, No. 9 (1920).

² Lamb and Larson, *THIS JOURNAL*, 42, 229 (1920); (b) MacInnes and Yeh, *ibid.*, 43, 2563 (1921); (c) Scatchard, *ibid.*, 47, 696 (1925).

A diagram of the arrangement of the electrodes and of the mica plate is presented in the figure, which also illustrates the shape of plate finally adopted. *M* is the type of electrode vessel developed for the calomel electrode as a simply made, convenient form for use with a flowing junction. *S* is the type of vessel employed either for the silver-silver chloride electrode used in testing the reliability and value of this type of junction, or for the antimony-antimony trioxide electrode to be discussed in a later paper;

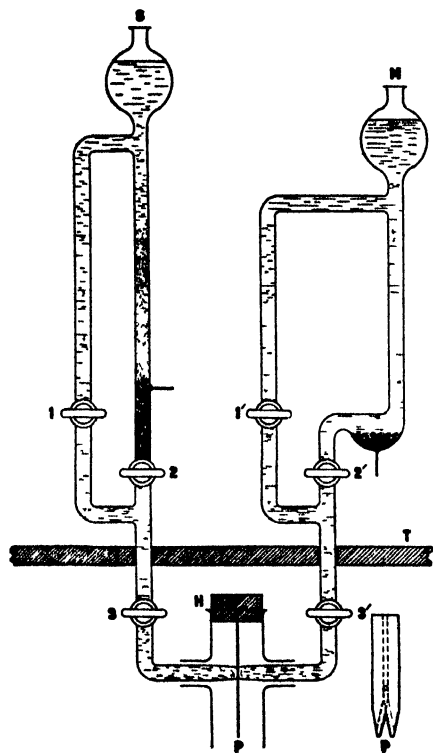


Fig. 1.—Arrangement of apparatus and detail of mica plate for liquid junction.

its length above the upper stopcocks is about 20 cm., the capacity of the bulb being 25–50 cc. The lower end of each vessel is bent horizontally, tapered, if necessary, to an internal diameter of 2–3 mm. and paraffined near the tip to obviate creeping of the liquid. These tips slip into side tubes in a glass tube *H* and are adjusted so that the issuing drops of liquid touch the mica plate *P*, conveniently held in a gash in a rubber stopper in *H*. The detail drawing of the plate shows its construction. A hole about 1 mm. in diameter is drilled in a thin strip of mica (about 1.5 by 7 cm.) by means of a glass-rod drill, working from both sides of the plate so that the edges are as smooth as possible; it is placed about 5 mm. below the exit tubes of the electrodes. The lower edge of the plate is notched and the faces are painted with hot paraffin, except for a narrow channel (indicated by dotted lines) past the

hole to one of the points, opposite points on the two sides; this insures that the only liquid junction is at the aperture in the plate.

The electrodes were kept in an air thermostat maintained at $25 \pm 0.02^\circ$, the exit tubes passing through the floor of the air chamber, *T*. The temperature of the surroundings was usually about 3° below that of the thermostat but the junction potentials encountered in the solutions investigated were sufficiently low so that changes due to fluctuations in the room temperature could be neglected. The cocks 3 and 3', attached to the electrodes by means of rubber tubing for convenience in filling the vessels, have their keys scratched near the bore at both ends, the scratches

being diametrically opposite, to facilitate the adjustment of the rate of flow. Cocks 2 and 2' serve for the thorough washing of the metal electrode with the electrolyte when the electrode is set up and at frequent intervals when it is in use but they are kept closed during the actual measurements, the by-pass cocks 1 and 1' being open. Before the mica plate is set in place the flow of the electrolytes is made as nearly equal as possible, 4-6 drops per minute being a suitable rate; then the plate is inserted and the exit tubes are brought against the opposite faces. The potential very quickly adjusts itself to a constant value, the time required being usually a matter of seconds and never more than a few minutes. Under favorable conditions (that is, small junction potentials) the variation in the potential proved to be less than 0.05 mv. over a period of several days.

The Liquid Junction Potential Between 0.1 *M* HCl and 0.1 *M* KCl at 25°

In order to test the accuracy and reproducibility of the junction potentials obtained with the device described, the potential between 0.1 *M* HCl and 0.1 *M* KCl, which has been investigated by MacInnes and Yeh,^{2b} was measured.

Preparation of Material

Silver.—Crystals of metallic silver were prepared by the rapid electrolysis of a solution of silver nitrate between small platinum wire electrodes, the anode being placed in a porous cup to prevent contamination of the metal with silver peroxide. The silver crystals were packed in a close mass around the platinum lead wire in the electrode vessel, held in place by a cotton plug at the bottom and covered with a layer of *crystalline* silver chloride about 10 cm. deep.

Silver Chloride.^a—Silver chloride was precipitated from a solution of silver nitrate by the addition of a solution of constant-boiling hydrochloric acid and the carefully washed precipitate dissolved in redistilled ammonium hydroxide. The resulting solution was filtered and the ammonia removed by absorption in sulfuric acid under a bell jar. The crystals of silver chloride were filtered and dried in a vacuum. The salt was protected from the action of light by a red lacquer coating on the electrode vessel and on the heating lamps of the thermostat. No appreciable darkening had occurred after five months' use of an electrode.

Mercury.—Mercury was purified by running it in a fine stream several times through a solution of mercurous nitrate and nitric acid, followed by distillation in a vacuum.

Calomel.—Pure mercury was dissolved in nitric acid, the mercury being present in considerable excess, and mercurous chloride precipitated by the addition of a solution of constant-boiling hydrochloric acid. After washing many times by decantation, the mixture of mercury and mercurous chloride was sucked dry on a Büchner funnel and shaken several days with water, changing the water every few hours. The material was kept under water in a brown bottle until required, when it was washed repeatedly with the particular solution to be used in the electrode under construction.

Potassium Chloride.—Ordinary "C. P." potassium chloride was recrystallized three times.

^a Crystalline silver chloride prepared by this method has been used by Professor J. N. Brønsted.

Hydrochloric Acid.—A strictly 0.1 *M* solution of hydrochloric acid was prepared by diluting a slightly stronger, carefully analyzed solution of the constant-boiling acid.

The following single electrodes were made up: (1) Ag, AgCl, 0.1 *M* HCl; (2) Ag, AgCl, 0.1 *M* KCl; (3) Hg, Hg₂Cl₂, 0.1 *M* KCl. The solutions used in all the electrodes were saturated with the corresponding metal chloride by shaking with an excess of the salt for from three to twelve hours in the thermostat before they were put into the electrode vessels. It is evident that the difference in potential between the first and second electrodes is a direct measure of the junction potential if the usual assumption is made that the activity of chloride ion in two fairly dilute solutions of equal ionic strength is the same. It is also apparent that there is no junction potential between the second and third electrodes and that the junction between the first and third is sensibly the same as between the first and second. Therefore, the difference in potential between the two possible cells comprising the calomel electrode as one pole is a measure of the junction potential. The experimentally determined potentials and their deviations over the period of observation are listed in Table I.

TABLE I

THE MEASURED POTENTIAL AT THE JUNCTION OF 0.1 *M* HCl AND 0.1 *M* KCl AT 25°

Cell	Potential, mv.	Mean deviation, mv.
Ag, AgCl, 0.1 <i>M</i> HCl 0.1 <i>M</i> KCl, AgCl, Ag	28.00	0.03
Ag, AgCl, 0.1 <i>M</i> HCl 0.1 <i>M</i> KCl, Hg ₂ Cl ₂ , Hg	73.3	.15
Ag, AgCl, 0.1 <i>M</i> KCl, Hg ₂ Cl ₂ , Hg	45.30	.05
(By difference)		
Ag, AgCl, 0.1 <i>M</i> HCl 0.1 <i>M</i> KCl, AgCl, Ag	28.00	

The difference in potential between a silver chloride electrode and a calomel electrode in the same chloride solution, the third cell in Table I, has been measured by Gerke⁴ for 1.0 *M* KCl and 1.0 *M* HCl. He obtained 45.5 mv. at 25°, which is in close agreement with our value of 45.3 mv. Both sets of measurements were made with finely divided crystalline silver electrodes but Gerke used the granular silver chloride obtained by direct precipitation. The value computed by Scatchard^{2c} from his revised activity data is 46.6 mv. The discrepancy between this last value and those obtained by direct measurement is probably due to the method of extrapolation used in deriving the activities, which is not entirely arbitrary, since Scatchard found excellent uniformity between silver electrodes prepared by three different methods—finely divided crystalline metal made electrolytically by Linhart,⁵ that obtained from the thermal decomposition of silver oxide by Noyes and Ellis,⁶ and his own electroplated platinum.⁷

⁴ Gerke, *THIS JOURNAL*, **44**, 1684 (1922).

⁵ Linhart, *ibid.*, **41**, 1175 (1919).

⁶ Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

⁷ Scatchard, *ibid.*, **47**, 641 (1925).

A summary of a number of values for the liquid junction potential is given in Table II.

TABLE II
COMPARISON OF VALUES FOR THE POTENTIAL AT THE JUNCTION OF 0.1 *M* HCl AND 0.1 *M* KCl AT 25°

	Potential, mv.
Measured directly	28.00
By difference	28.00
Measured directly, MacInnes and Yeh	26.78
Computed, Lewis and Sargent formula	28.4

It will be observed that our value is greater than that found by MacInnes and Yeh, lying between the value of the latter authors and that computed by the Lewis and Sargent formula,⁸ $E_j = RT/F \ln \Lambda/\Lambda'$. The ratio of the equivalent conductances of 0.1 *M* HCl and 0.1 *M* KCl, Λ/Λ' , calculated from our measured value of the junction potential, E_j , is 2.974. From the conductance data given by MacInnes and Yeh this ratio is 3.026. The difference, 1.7%, is far too great to be accounted for by any probable error in the conductivity measurements. It seems most plausible to ascribe the discrepancy to the abnormality of the potassium ion pointed out by MacInnes and Yeh, who found good correspondence between the calculated and measured junction potentials at the boundaries of a number of univalent chloride solutions except in the presence of potassium ion.

The reproducibility of the potentials at the liquid junctions formed in the manner described is certainly within 0.2 mv.; with regard to the absolute accuracy no definite statement can be made. The extreme simplicity of the arrangement, the ease and rapidity with which it can be set up and the fact that a small volume of liquid suffices for quite an extended series of measurements may be emphasized. Moreover, it eliminates the necessity of maintaining the column heights in the two arms of the cell in inverse ratio to the densities of the electrode solutions to insure equal rates of flow, a marked advantage over other forms of flowing junction.

In conclusion the authors wish to acknowledge their indebtedness to Dr. John Johnston for many valuable suggestions in connection with this work.

Summary

A simple arrangement for obtaining reproducible liquid junction potentials between two flowing electrolytes is described and its applicability tested by determining the potential at the boundary of 0.1 *M* HCl and 0.1 *M* KCl. The result obtained is in satisfactory agreement with that computed from the theoretical equation of Lewis and Sargent and in fair accord with the measured value of MacInnes and Yeh.

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⁸ Lewis and Sargent, *THIS JOURNAL*, **31**, 363 (1909).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE HEAT OF FORMATION OF ZINC OXIDE

BY GEORGE S. PARKS, CHARLES E. HABLUTZEL AND LAWRENCE E. WEBSTER

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The data in the literature for the heat of formation of zinc oxide are extremely discordant. Thus Mellor¹ gives ten values ranging from 86,900 cal. (Andrews, 1852) to 82,970 cal. (the lowest result of de Forcrand, 1902). Of these the results of de Forcrand are the latest and probably the most reliable. More recently Parr and Moose² have reported the value 84,900 cal., obtained by direct combination of the elements, and Maier and Ralston³ have calculated the values, 82,830 and 83,097 cal., from equilibria measurements and from thermal data, respectively. In view of this situation the present investigation was undertaken.

Richards and Burgess⁴ have determined the heat of solution of zinc in hydrochloric acid. In the present case we have measured the heat of solution of zinc oxide under precisely comparable conditions. These two heats of solution, combined with the heat of formation of water, serve as a basis for the calculation of a very reliable value for the heat of formation of zinc oxide from its elements.

Experimental Part

Richards and Burgess in their experiments dissolved 7.5 g. of zinc in 941.4 g. of hydrochloric acid of the strength 1HCl-20H₂O (approximately 2.633 *N*). We accordingly prepared acid of this concentration and in six series of determinations measured the heat effect observed when 25.83 g. of zinc oxide was dissolved in 2605 g. of acid. Thus the resulting solutions in our experiments had the same concentration of hydrochloric acid and zinc chloride as those obtained by Richards and Burgess.

As a calorimeter for the measurement of the heat of solution we used a Pyrex Dewar jar of 3 liters' capacity, for which a thin cover of cork, coated with paraffin, was made. Three small holes were punched in this cover for the stirrer, for the Beckmann thermometer and for the introduction of the zinc oxide. The glass stirrer was of the propeller type, with eight blades, and gave adequate circulation when operated at about 200 r.p.m. The Beckmann thermometer had been calibrated by the United States Bureau of Standards immediately before the measurements. The heat capacity of the apparatus as a whole was measured first in a series of nine determinations by an electrical method and subsequently in a series

¹ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, vol. 4, p. 512.

² Parr and Moose, *THIS JOURNAL*, **46**, 2660 (1924).

³ Maier and Ralston, *ibid.*, **48**, 371 (1926).

⁴ Richards and Burgess, *ibid.*, **32**, 431 (1910).

of five determinations by a rough method of mixtures, the respective mean results being 182 and 185 calories per degree. Accordingly we have used 183 calories in our calculations. For the specific heat of the acid the value of Richards and Rowe,⁵ 0.8486 cal./g., was assumed.

In some preliminary experiments with our apparatus it was found that a small part of the oxide had a tendency to cake at the bottom of the Dewar jar and thereby took considerable time to go into solution. This difficulty seemed to be due entirely to the shape of the bottom of the jar and was remedied by introducing about a kilogram of mercury into the container. The mercury took no part in the reaction⁶ and, as its specific heat was known, a correction of about 36 calories per degree was added to the heat capacity of the apparatus as previously found. Under these conditions the 25.83 g. of zinc oxide went into solution within a period of five minutes, with a temperature rise of about two degrees above the initial temperature, 18.0°. The Regnault-Pfaundler method was employed in determining the cooling corrections during the solution process and the usual calorimetric precautions were observed throughout the measurements. The reproducibility of the results thus obtained is illustrated by the fact that the nine consecutive runs on Sample I showed an average deviation of 15 calories (0.10%) from the mean value, the maximum deviation being 35 calories (0.23%).

The zinc oxide samples were prepared from Baker's c. p. materials, made by the "wet process" and "dry process," respectively. The manufacturer's analyses as well as subsequent analyses made in this Laboratory indicated that the total impurities were much less than 0.1% in all instances. Sample I was "wet-process" oxide which had been dried on a hot-plate at about 110° for 24 hours. Samples II and III were a similar material which had been heated for 24 hours in an electric furnace at 500° and 800–1000°, respectively. This process of heating at high temperatures caused considerable shrinkage in the apparent volume of the oxide. Sample IV was "dry-process" oxide which had been dried on a hot-plate at 110° for 24 hours and Sample V was similar material heated at 500° for 12 hours. These last two samples occupied a larger volume per gram and apparently were much more finely divided than the corresponding ones prepared from the wet-process product. Sample VI was "recrystallized" oxide, made by sealing dry-process material into an evacuated (0.01 mm.) silica flask and heating to approximately 1100° for about 60 hours.⁷

The following table summarizes our results for the heat of solution of these six samples of zinc oxide in acid of the strength 1HCl-20H₂O. The data are expressed in terms of the 18° calorie for a final temperature of 20.0°.

⁵ Richards and Rowe, *Proc. Am. Acad. Arts Sci.*, **43**, 475 (1908).

⁶ As a matter of fact, in a number of determinations, including about half of those in Series IV, the mercury was omitted. The results obtained in these cases showed no essential differences from the others, although a somewhat longer time interval was required for complete solution of the oxide.

⁷ Numbers VI and IV were identical with "samples 2 and 3," respectively, employed in some previous heat-capacity determinations (Maier, Parks and Anderson, *This Journal* **48**, 2572 (1926)).

Dixon,⁵ Flügel,⁶ Adams,⁷ Harkins⁸ with students, Randall and Vanselow⁹ and Hovorka and Rodebush,¹⁰ Bedford,¹¹ and Barnes, Archibald and McIntosh¹² used a differential platinum thermometer and Griffiths,¹³ as long ago as 1891, employed the platinum thermometer for boiling- and freezing-point determinations.

The second development is that of improving the determination of concentration. Roloff¹⁴ was the first to analyze his solution after a large amount of solid solvent had separated. Some method of analyzing the solution in equilibrium with the solid solvent has been used in all of the modern determinations. The same end was accomplished by Walker and Robertson¹⁵ and by Richards¹⁶ when they mixed the solution with pieces of ice. This method has distinct advantages, as enumerated in the latter paper.

The most careful determinations of the freezing point of dilute solutions of hydrochloric acid by Randall and Vanselow⁹ include these improvements and constitute, with those of Hovorka and Rodebush,¹⁰ the most refined experiments reported.

The purpose of the present experiments was to extend the results to more concentrated solutions. The activity coefficients as calculated by the methods of Lewis and Randall¹⁷ are also reported.

Experimental Procedure

Temperature intervals were measured with a platinum thermometer and Wheatstone bridge manufactured by the Leeds and Northrup Company. The thermometer and bridge were standardized by the Bureau of Standards, the thermometer having a resistance in melting ice, (R_0), of 25.246 international ohms, a fundamental interval (F. I.) of 9.8059 ohms, a value of δ (in the Callendar formula) of 1.509 and an accuracy of 0.01% in the measurement of temperature intervals. The bridge was certified to be reliable to 0.00005 ohms under specified conditions. The bridge was maintained at a constant temperature within 0.1° by a suitable thermostat. A current of approximately 3 milli-amperes was used through the thermometer. As a consequence of the precautions taken, none of the connections being changed during the experiments and the

⁵ Dixon, *Sci. Proc. Roy. Dublin Soc.*, **13**, 49 (1911).

⁶ Flügel, *Z. physik. Chem.*, **79**, 577 (1912).

⁷ Adams, *THIS JOURNAL*, **37**, 481 (1915).

⁸ Harkins *et al.*, *ibid.*, **38** (8 papers), 2643-2717 (1916).

⁹ Randall and Vanselow, *ibid.*, **46**, 2418 (1924).

¹⁰ Hovorka and Rodebush, *ibid.*, **47**, 1614 (1925).

¹¹ Bedford, *Proc. Roy. Soc. (London)*, **83A**, 454 (1910).

¹² Barnes, Archibald and McIntosh, *THIS JOURNAL*, **27**, 47 (1905).

¹³ Griffiths, *ibid.*, **48**, 220 (1891) [through *Jour. Chem. Soc.*, **60**, ii, 251 (1891)]; also Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

¹⁴ Roloff, *Z. physik. Chem.*, **18**, 572 (1895).

¹⁵ Walker and Robertson, *Proc. Roy. Soc. Edinburgh*, **24**, 363 (1903).

¹⁶ Richards, *Z. physik. Chem.*, **44**, 563 (1903); *THIS JOURNAL*, **25**, 291 (1903).

¹⁷ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chapter 27.

battery and galvanometer circuits including mercury-cup switches, the recorded temperature intervals should be accurate to 0.0005° , making certain the third decimal figure.

The temperatures were calculated by the Callendar formula

$$pt = \frac{R_t - R_0}{FI} \times 100$$

$$t - pt = \delta \left(\frac{t}{100} - 1 \right) \left(\frac{t}{100} \right)$$

where t is the temperature in Centigrade degrees and pt the "platinum temperature."

The apparatus in which the freezing mixture was maintained consisted of an unsilvered Dewar cylinder of Pyrex glass approximately 24 cm. deep with an inside diameter of 5 cm. It was fitted with a rubber stopper holding the thermometer, a stirrer,

4.0

3.9

3.8

3.7

3.6

3.5

1.0 2.0 3.0 4.0
Depressions of freezing point (θ).

The data of Richards and Jackson are represented by squares; those given in Landolt and Börnstein's "Tabellen" by triangles, and those of Randall and Vanselow by circles.

Fig. 1.—The change of the ratio θ/m plotted against θ ; the depressions of the freezing point are plotted as abscissas, the ratios as ordinates.

a tube for the withdrawal of a sample of solution and a tube by which the system could be evacuated or pressure applied. The tube for the removal of the sample extended to a depth about three-quarters down the coil of platinum wire in the thermometer and terminated in a small bulb filled with glass wool to prevent the passage of any small pieces of ice.¹⁸ The sample of solution was removed by applying a pressure of clean air, thus avoiding the possibility of losing material in the form of a vapor. This precaution is not so important in the case of solutions of hydrochloric acid as if the solute had an appreciable vapor pressure, when an indeterminate amount of material would be lost if suction was applied.

¹⁸ For a similar device, see Richards and Fraprie, *Proc. Amer. Acad. Arts Sci.*, **36**, 507 (1901).

The Dewar cylinder was immersed in an agitated bath of ice and salt solution whose concentration was regulated so that the temperature was maintained slightly below that inside the Dewar cylinder.

The water used had been thrice distilled (freed from organic matter, ammonia and carbon dioxide). A sample prepared on the day previous to the experiment was boiled for about two hours to free it from dissolved air, then stoppered in a Pyrex flask and chilled to 0°, cooling under its own vapor. Precautions to prevent the solution of air are necessary, for its solubility may be different in water than in the hydrochloric acid. Randall and Vanselow seem to be the first to report precautions of this nature.

The ice was prepared from a commercial product by shaving—thereby producing a finely divided solid that would make a mush with water—washed three times, finally with the best water. Clear pieces of ice were selected for the preparation of the sample. When this ice was mixed with the water, air was held mechanically in the interstices. This was immediately removed by suction. Precaution was taken to prevent the melting of the ice during the whole manipulation. The temperature of this freezing mixture corresponded well within 0.001° with a mixture of water and ice prepared by supercooling a sample of the best water and then shaking.¹⁹

The hydrochloric acid was prepared from C. P. acid by fractionally distilling three times, the middle portion being used each time. A final distillation, to remove any dissolved glass, was made just before the experiment. The all-Pyrex distilling apparatus had been used with hydrochloric acid many times. This acid was chilled before introduction into the freezing mixture.

The procedure during a determination was as follows. The washed ice was mixed with the water and evacuated several times to remove air held in the ice and then evacuated again for twenty minutes after the thermometer had been introduced and the apparatus assembled. The pressure was then released and the mixture stirred. The resistance of the thermometer in this ice-bath was determined each day and taken as R_0 . A sufficient amount of acid was then added, the system evacuated for about fifteen minutes after a brief preliminary stirring and the resistance of the thermometer measured again (at atmospheric pressure). With a suitable regulation of the temperature in the outside bath, this equilibrium temperature would remain constant within the accuracy of the thermometer for some time. After about five minutes of constant temperature, a final reading was made and the sample withdrawn by applying pressure.

This sample, of approximately 40 cc., was divided into two portions, weighed and analyzed gravimetrically by precipitating and weighing as silver chloride. All weights were reduced to vacuum. The concentrations, expressed in gram equivalents per 1000 g. of solution (6.9764 wt. AgCl/wt. solution) and thence the molality (m , the gram equivalents per 1000 g. of solvent), were calculated using the molecular weight of hydrochloric acid as 36.466.

A second point was obtained by adding more chilled water and acid and repeating the technique. Not more than three points were obtained on the same day. The concentrations were so chosen that the determinations

¹⁹ Ref. 10, p. 2426.

of one day would overlap those of another day, thus producing verifications of previous experiments.

The results are given in Table I. The first column gives the number of the experiment; the second the molality, (m); the third the temperature lowering, (Θ), or the freezing point in degrees below Centigrade zero; and the fourth the ratio of temperature to molality, (Θ/m).

TABLE I
THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

No.	m	Θ	Θ/m
1	0.08321	0.2934	3.526
2	.1427	.5033	3.527
3	.2024	.7145	3.530
4	.2198	.7771	3.538
5	.2374	.8440	3.554
6	.3080	1.1000	3.571
7	.3137	1.1202	3.571
8	.4082	1.4738	3.610
9	.5275	1.9344	3.666
10	.6363	2.3664	3.719
11	.6785	2.5465	3.753
12	.6969	2.6114	3.747
13	.7736	2.9420	3.803
14	.8187	3.1219	3.813
15	.8945	3.4545	3.862
16	.9765	3.8192	3.911
17	1.0324	4.0721	3.944

Of these determinations, three are inconsistent with the rest, namely, numbers 5, 11 and 13. They have not been considered in subsequent calculations.

The ratio Θ/m is plotted as ordinate against Θ as abscissa in Figure 1. Data as enumerated in Landolt-Börnstein's "Tabellen,"²⁰ as well as those of Richards and Jackson²¹ and a few of Randall and Vanselow's are plotted for comparison.

Theoretical Calculations

From these data can be calculated by the graphical methods of Lewis and Randall²² the mean activities of the ions and the activity coefficients. The latter can be compared with those calculated by Lewis and Randall²³ from the e.m.f. measurements of Linhart²⁴ and those of Scatchard.²⁵

The graphical method of calculating the "preliminary activity co-

²⁰ Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th ed., 1923, Vol. II, p. 1441.

²¹ Richards and Jackson, *Proc. Am. Acad. Arts Sci.*, **41**, 451 (1906).

²² Ref. 17, Chapters 23 and 27.

²³ Lewis and Randall, *THIS JOURNAL*, **43**, 1112 (1921).

²⁴ Linhart, *ibid.*, **39**, 2601 (1917); **41**, 1175 (1919).

²⁵ Scatchard, *ibid.*, **47**, 641 (1925).

efficient" (γ'), that applying to the temperature of the freezing mixture and uncorrected for the heat of solution, necessitates the evaluation of areas under curves from infinite dilution to the concentration in question. The value of $\gamma_{25^\circ} = 0.819$ for $m = 0.070$, as interpolated from Scatchard's data, was accepted in order to evaluate the area for more dilute solutions. If the value of $\gamma_{25^\circ} = 0.824$ (interpolated from Randall and Vanselow's data) is used, the results are correspondingly higher.

The calculation of the factor by which the "preliminary activity coefficient" must be multiplied to give the corrected activity coefficient at 25° requires a knowledge of heat data, all of which are not available in the literature. The values for the partial molal heat capacities (\overline{c}_p) were taken from the paper of Randall and Ramage,²⁶ while those for the partial molal heat content of the solvent (\overline{L}_1) were very generously supplied by Professor Merle Randall.²⁷ The results of these calculations are given in Table II.

TABLE II
COMPARISON OF THE ACTIVITY COEFFICIENTS*

m	γ'	γ/γ'	γ_{25° , F.P.	γ_{25° , S.	γ_{25° , L. and R.
0.1	0.803	0.996	0.800	0.801	0.804
.2	.780	.992	.774	.774	.783
.3	.773	.987	.763	.763	.768
.4	.774	.983	.761	.760	.763
.5	.781	.980	.765	.763	.762
.6	.789	.977	.771	.770	.770
.7	.800	.974	.779	.777	.782
.8	.812	.971	.788	.789	.794
.9	.830	.968	.804	.802	.808
1.0	.848	.965	.818	.817	.823

* If the value of Randall and Vanselow of $\gamma_{25^\circ} = 0.824$ at $m = 0.070$ is used, the final values of γ_{25° become 0.779 at $m = 0.2$, 0.766 at $m = 0.4$, 0.776 at $m = 0.6$, 0.793 at $m = 0.8$ and 0.823 at $m = 1.0$.

The first column of Table II gives the molality; the second the "preliminary activity coefficient" (γ') at the temperature of the freezing point of the solutions and uncorrected for the change in heat content; the third column the factor by which the "preliminary" values are multiplied to give the activity at 25° and calculated from the thermal data. The fourth, fifth and sixth columns compare the final activity coefficients at 25° as calculated from the freezing points, from the e.m.f.'s by Scatchard and from e.m.f.'s as calculated by Lewis and Randall. The agree-

²⁶ Randall and Ramage, *THIS JOURNAL*, 49, 99 (1927).

²⁷ Unpublished data. The values were

$m =$	0.2	0.4	0.6	0.8	1.0
$\frac{\overline{c}_p - \overline{c}_{p_1}}{\overline{L}_1}$	-.0075	-.021	-.039	-.062	-0.084
	-.33	-1.1	-2.0	-3.1	-4.6

ment is quite satisfactory. Similar data for solutions up to 0.1 *M* have been discussed by Scatchard.²⁸

The writer wishes to express his indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing mechanical aid in the calculations.

Summary

A report is made of the determination of the freezing points of aqueous solutions of hydrochloric acid up to a concentration of 1.0 molal, making use of a platinum thermometer as a temperature measuring device.

The activity coefficients are calculated and compared with those derived from electromotive force measurements.

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[CONTRIBUTION FROM THE LABORATORY OF THE LINDE AIR PRODUCTS COMPANY]

SOME PHYSICAL PROPERTIES OF VINYL CHLORIDE

BY L. I. DANA, J. N. BURDICK AND A. C. JENKINS

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Although vinyl chloride (C_2H_3Cl) has been known as a chemical compound for a number of years, owing to the difficulties attending its preparation and purification, relatively little exact work has been done with it. Recent progress in chemical synthesis has made this material available in quantity commercially and therefore it has seemed worth while to review previous work on the subject in order to ascertain the present state of knowledge of the properties.

Beyond a few scattered values of the boiling point of vinyl chloride, very little has been published concerning its physical properties. Recently the desirability of utilizing vinyl chloride as a refrigerating fluid (boiling point -13.9°) has been suggested, and hence it has appeared desirable to conduct an experimental determination of its most important physical properties. In this investigation the measurements of the vapor-pressure curve, liquid densities and freezing point are reported; in addition a few of its other physical properties have been estimated from theory.

Description of Experiments

Vapor-Pressure Curve.—Commercial samples of vinyl chloride¹ were obtained in small steel cylinders. This liquid was purified by fractional distillation in a vacuum insulated, low-temperature Hempel column and was further subjected to a fractional distillation in a closed, low-

²⁸ Scatchard, *THIS JOURNAL*, **47**, 641 (1925). See also LaMer, *Trans. Amer. Electrochem. Soc.*, **51**, (1927), preprint No. 58; and Van Laar, *Z. anorg. allgem. Chem.*, **139**, 108 (1924).

¹ Material obtained from the Carbide and Carbon Chemicals Corporation, New York City.

temperature fractionation apparatus, operated with a Langmuir pump in series for the purpose of removing the traces of moisture and all non-condensable gases. Finally, the samples were tested for boiling range and pressure drop in the vapor-pressure apparatus mentioned below. On distilling off over 95% of the sample at constant temperature, the pressure drop was found to be less than 2 mm. in 760 mm. of Hg, and on distilling off at constant pressure the temperature drop was less than 0.05°. It is probable that the purity was higher than 99.9%.

The vapor pressures were measured over the temperature range from -28 to 60°, corresponding to a pressure range of 40 to 760 cm. of Hg absolute or from 0.5 to 10 atm. absolute. Below and around one atmosphere a mercury manometer, with a vacuum over one arm, was employed for the pressure measurement. From one to five atmospheres a tall mercury manometer was used, while above this pressure a dead-weight piston gage served to measure the pressure. Various forms of containers for the sample were used. In general the experimental technique was similar to that used in the measurement of the vapor pressures of some paraffin hydrocarbons,² to which work reference is made for experimental details.

The boiling point at one atmosphere was determined a number of times and was found to be -13.9, $\pm 0.1^\circ$. Biltz³ gives the boiling range as -18 to -15°, which would seem to be much too low temperatures and too wide a range to correspond with the pure material tested in this investigation. In the following table are given the values of the pressures and corresponding temperatures observed for the vapor pressures.

TABLE I
VAPOR PRESSURES OF VINYL CHLORIDE

Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg
-28.73	39.56	4.01	149.06	39.72	450.0
-23.02	51.30	5.53	158.2	46.80	543.4
-16.61	67.76	16.21	225.8	54.87	667.6
-13.61	76.75	25.72	302.7	60.34	758.6
- 8.32	94.90	33.53	378.9	60.34	760.3
- 1.57	122.48	39.72	449.2		

The experimental observations have been combined into the well-known Nernst⁴ equation of the form

$$\log p = a + b/T + 1.75 \log T + cT$$

in which the pressure p is expressed in atmospheres absolute and the temperature T in degrees centigrade absolute. The values for the constants are as follows

$$a = 0.8420; \quad b = -1150.9; \quad c = -0.002415$$

² Dana, Jenkins, Burdick and Timm, *Refrigerating Eng.*, 12, 387 (1926).

³ Biltz, *Ber.*, 35, 3525 (1902).

⁴ Nernst, "Theoretical Chemistry," Macmillan Co., New York, 1923, p. 815.

On the average the agreement of the observed results with those computed by the formula is within the experimental error, 0.3%.

Liquid Densities.—The method employed for the determination of the liquid densities has been described in an earlier paper by the authors,⁴ and is similar to that used by the Bureau of Standards on ammonia.⁵ Preliminary experiments were first made in a Pyrex pycnometer in which only the coefficient of expansion of the liquid was measured, since the weight of liquid vinyl chloride in the pycnometer was not ascertained. The final measurements were made with the pycnometer, shown in Fig. 1, constructed of Jena 16^{III} glass. After calibrating the pycnometer carefully with mercury, the sample was condensed in and the pycnometer sealed off. Readings of the liquid in the stem were observed at various temperatures from -13 to 60° in a thermo-regulated bath and the temperatures were read by a platinum resistance thermometer. By weighing the pycnometer full and empty, the corrected weight of vinyl chloride was found to be 5.9716 g. Enough data were then available for computing the absolute density. The results for the coefficient of expansion agreed to 0.1% with those obtained with the Pyrex pycnometer.

Correction has to be applied for the quantity of vapor in the vapor space above the liquid in the pycnometer. No experimental values for the vapor densities are available, however, so that these values were computed theoretically. Since, however, the maximum value for this correction is about 0.15% and an accuracy

⁴ Cragoe and Harper, Bureau of Standards, Scientific Paper, No. 420.

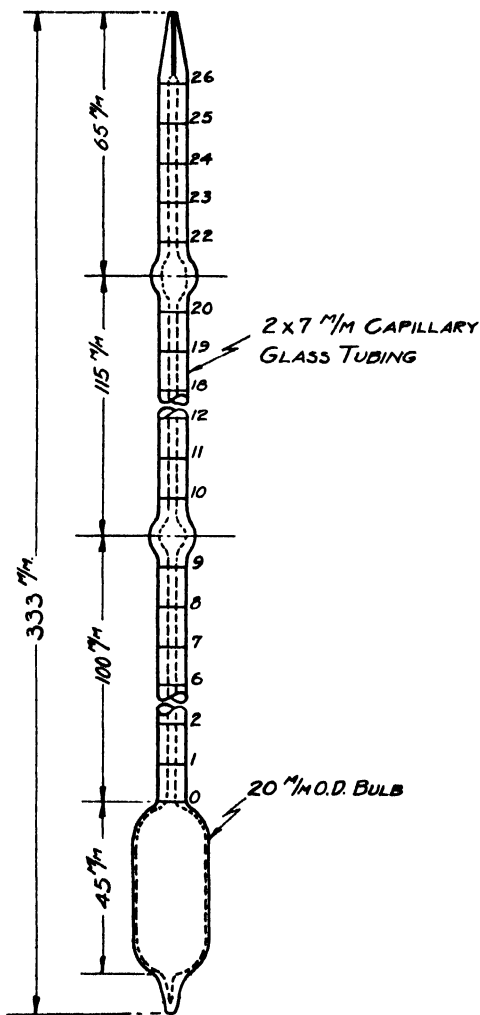


Fig. 1.—Piezometer for liquid densities.

of 0.1% is claimed for the results, it is evident that an accuracy of 50% for the vapor density correction is sufficient. It is believed that the vapor density can be computed with much higher accuracy and as a matter of interest this has been done and the results are given later on.

RESISTANCE THERMOMETER

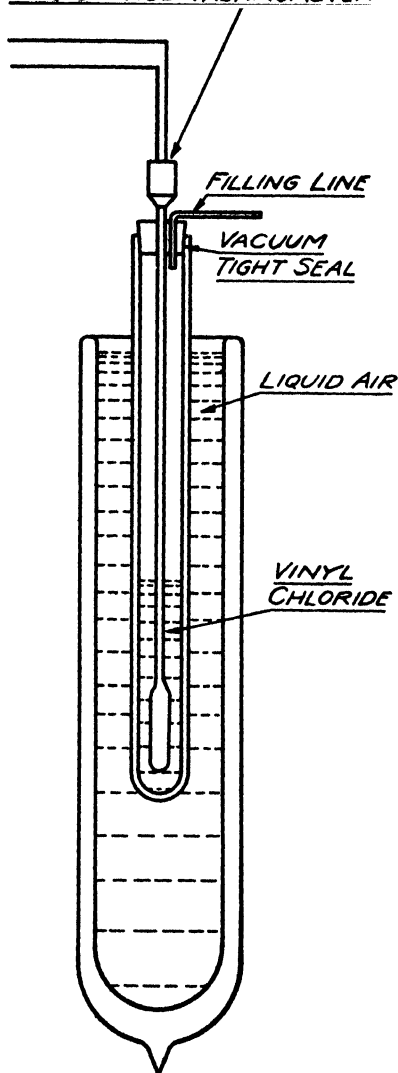


Fig. 2.—Freezing-point apparatus.

The liquid densities of vinyl chloride are shown in Table II.

It is believed that the results are good to 0.1%.

An empirical formula representing the results from -13 to 60° is as follows

$$d = 0.9471 - 0.001746t - 0.00000324t^2$$

in which d is the liquid density in grams per cc. and t is the temperature in degrees centigrade. The data agree with the formula to better than 0.1%.

Freezing Point.—Since relatively large quantities of vinyl chloride, purified by fractional distillation for the vapor-pressure measurements, had been prepared, it was decided to determine the freezing point by direct immersion of the thermometer in a large sample. The apparatus is shown in Fig. 2. Throughout the measurements the sample was handled in a closed system to keep out moisture. Liquid air was employed as the cooling medium. With a single tube the rate of cooling was too rapid; hence a double-walled tube was used. This also had the effect of producing a uniform temperature gradient in the freezing-point sample. Preliminary determinations with a calibrated, propane filled, low temperature thermometer resulted in the value -159° . The final and most accurate determination was made with a platinum resistance thermometer which had previously

been calibrated at the freezing point of mercury, the sublimation point of carbon dioxide and the boiling point of oxygen.² The period of freezing lasted about seven minutes and the freezing temperature was

constant to within 0.1° at -159.7° . Considering the purity of the sample it is safe to claim an accuracy of 0.1° for this freezing point.

TABLE II
LIQUID DENSITIES OF VINYL CHLORIDE

Temp., $^\circ\text{C.}$	Liquid density, g./cc.	Temp., $^\circ\text{C.}$	Liquid density, g./cc.
-12.96	0.9692	39.57	0.8733
1.32	.9443	48.20	.8555
13.49	.9223	59.91	.8310
28.11	.8955		

Estimated Vapor Densities and Latent Heats

Since the vapor densities were required for correction terms to the liquid densities, it appeared worth while to estimate them as accurately as possible so that the values might be of use elsewhere. At the same time, since the vapor-pressure curve was measured, the latent heats could be estimated with the aid of Clapeyron's equation.

Unfortunately the critical constants of vinyl chloride are not known so that the law of corresponding states could not be employed directly; but van Laar⁶ has described methods based on empirical relationships by means of which the critical constants may be computed, which in turn serve in other relationships from which the specific volumes can be ascertained. By these methods the estimated critical pressure is 52.2 atm. while the estimated critical temperature is 142° .

In the following table the estimated specific volumes of the saturated vapor, estimated by the method of van Laar, are given.

TABLE III
ESTIMATED SPECIFIC VOLUMES OF SATURATED VAPOR OF VINYL CHLORIDE

Temp., $^\circ\text{C.}$	Spec. vol., cc./g.	Temp., $^\circ\text{C.}$	Spec. vol., cc./g.
-30	635	20	105.4
-20	418	30	79.7
-10	284	40	60.3
0	199	50	46.3
+10	143.3	60	36.2

To compute the latent heats the above values for the specific volumes were used and the slopes of the vapor-pressure curve were determined graphically.

The latent heats were also computed by means of the law of corresponding states, comparing with the values given by Holst⁷ for methyl chloride. At the boiling point the values by the two methods agree to 1%, while at 50° they agree to 5%.

⁶ Van Laar, "Die Zustandsgleichung," Leopold Voss, Leipzig, 1924, pp. 186, 21.

⁷ Holst, *Comm. Phys. Lab. Univ. Leiden*, No. 144c.

TABLE IV
ESTIMATED LATENT HEATS OF VINYL CHLORIDE

Temp., °C.	Slope of vapor-pressure curve, cm. of Hg/°C.	Latent heat, cal./g.	
		By Clapeyron's equation	By corresponding states
-20	25.4	88.4	85.7
-10	35.4	84.1	84.1
0	47.1	81.2	83.0
+10	61.8	79.8	81.7
20	79.7	77.7	80.2
30	100.2	76.2	78.5
40	124	73.2	76.6
50	151	70.1	74.4

Summary

The vapor pressure of vinyl chloride was measured from -28 to 60°. The normal boiling point was found to be -13.9, $\pm 0.1^\circ$.

The liquid densities were measured over the temperature range -13 to 60°.

The freezing point was found to be -159.7, $\pm 0.1^\circ$.

Estimated values of the vapor densities and latent heats were computed from theoretical relationships.

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NOTE

Calculation of Heats of Combustion.—Kharasch and Sher¹ have applied the electronic conception of valence to the calculation of heats of combustion of organic compounds. They find that the energy change which accompanies the displacement of one valence electron from the position which it occupies in methane, a carbon chain or the benzene nucleus to the position after combustion in carbon dioxide is 26.05 kg. cal. per mole. Thus the heat of combustion of a hydrocarbon is given by the product $26.05 \times N$, where N is the number of electrons displaced.² Electrons associated with bonds other than C—C and C—H are accompanied by an additional energy change during combustion. To the term $26.05 N$, Kharasch and Sher add 26 kg. cal. for each aliphatic ether group, 13 kg. cal. for each ethylenic linkage, primary alcohol, ester or aromatic ether group and 6.5 kg. cal. for each secondary alcohol or ketone group. No correction is added for tertiary alcohol, phenol or acid groups. In most cases this method gives good results, but for aromatic compounds the calculated values are uniformly higher than the experimental values and the

¹ Kharasch and Sher, *J. Phys. Chem.*, 29, 625 (1925).

² Each bond corresponds to two electrons. In oxygen compounds the two oxygen bonds are disregarded. Thus N is 8 for methane, 30 for benzene, 58 for phenyl benzoate, etc.

deviations become greater as the number of benzene nuclei increases. This necessitates a correction for each benzene nucleus. The method proposed for this correction follows.

The electrons associated with three of the bonds of the benzene nucleus (μ electrons) will be assumed to differ in energy relations from those of the other twelve (λ electrons).³ There is an energy change of 24.85 and 26.05 kg. cal. per mole, respectively, for each μ and λ electron present in the compound being burned. The heat of combustion in kg. cal. per mole at constant pressure of compounds containing C and H, or C, H and O, is given by the equation⁴ $Q_p = 26.05\lambda + 24.85\mu + 22.7$ for each ether group + 19.5 for each aldehyde group + 13 for each ethylenic linkage, primary alcohol or ester group + 6.5 for each secondary alcohol group + 3.2 for each phenol or tertiary alcohol group + 0.0 for each acid or ketone group.

Of the 57 aromatic compounds containing C and H, or C, H and O, whose heats of combustion were calculated by Kharasch and Sher, the new method gives results closer to the experimental values in 37 cases and the same in 7 cases. The average per cent. difference between experimental and calculated values is lowered from 0.52 to 0.32%. Table I shows per cent. difference between calculated and experimental values for 171 aromatic compounds of different types.

TABLE I

DIFFERENCE BETWEEN CALCULATED AND EXPERIMENTAL HEATS OF COMBUSTION

Aromatic compounds containing C and H, or C, H and O	No. of calculations	Difference between calculated and experimental values	
		Total %	Average %
Saturated hydrocarbons	26	8.4	0.32
Ethylenic hydrocarbons	11	2.7	0.25
Phenols	24	10.7	0.44
Ethers	22	8.0	0.36
Aldehydes	12	7.3	0.61
Ketones	15	5.5	0.37
Acids	33	13.3	0.40
Esters	28	8.3	0.30
Total	171	64.2	0.37

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³ See Pauling, *THIS JOURNAL*, **48**, 1132 (1926).

⁴ λ and μ are the numbers of λ and μ electrons present. In aliphatic compounds there are no μ electrons and λ is the same as N in Kharasch and Sher's equation. Each benzene nucleus contains 6 μ electrons. Thus $\lambda = 38$ for hexane; $\lambda = 48$, $\mu = 18$ for anthracene; $\lambda = 46$, $\mu = 12$ for phenyl benzoate, etc.

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMICAL LABORATORY, LEHIGH UNIVERSITY]

RATE OF REACTION BETWEEN BROMINE AND UNSATURATED FATTY ACIDS AS EVIDENCE OF STEREO-ISOMERISM¹

BY CALVIN A. KNAUSS AND JUDSON G. SMULL

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Various studies on the action of bromine toward unsaturated fatty glycerides indicated that the rate of reaction was dependent upon several factors. Thus, the nature and dilution of the solvent has a marked effect on the rate of bromination.

Working under the same conditions with respect to solvent, the rate of bromination was applied to glycerides of oleic, linolic and linolenic acids, respectively, and to the free fatty acids of the respective glycerides. The rate of bromination was found to vary with the different unsaturated fatty acids.

The effect of ultraviolet light during the bromination was also studied, with the result that certain stereo-isomers of unsaturated acids were determined which escaped detection by the present methods of analysis.

In an investigation the authors have undertaken dealing with the stereo-isomers of linolenic acid they observed that in the bromination of the fatty acids of linseed and other oils several factors seemed to influence the addition of the bromine to the unsaturated acids as, for example, the concentration of the solvent, the composition of the fatty acids and light. A supposedly pure sample of linolenic acid was found to have an iodine number of 223 by the Wijs method and a hexabromide number of 46, while the theoretical number is 274.3. Erdman and Bedford reported an iodine number of 227 for linolenic acid. It is very difficult to explain these discrepancies but when it is considered that the *cis* modifications of stereo-isomeric compounds generally react with bromine only with difficulty, a new view of this phenomenon may be taken. The authors are certain that linolenic acid is present in linseed oil in several stereo-isomeric forms (this work is to be reported in a later paper), so that an explanation of the erratic action of the fatty acids of drying oils may be found from a stereochemical consideration of this problem.

Historical

A survey of the literature has shown that although the iodine number of oils is an important characteristic, very little work has been reported on halogenation of fatty acids aside from the methods for the determination of iodine number.

McIlhiney² reported a method of bromination which he advocated as a

¹ Presented before the Paint and Varnish Division of the American Chemical Society at its 73rd meeting, Richmond, Virginia.

² McIlhiney, *THIS JOURNAL*, 21, 1084 (1899).

substitute for the iodine methods. He used a *N*/3 solution of bromine in carbon tetrachloride, allowed the solution to stand for only two minutes, then added potassium iodide and titrated with sodium thiosulfate. After this titration was finished, neutral potassium iodate solution was added and the liberated iodine, equivalent to free hydrogen bromide, was titrated and calculated as the substitution.

Cerdeiras³ has studied the rate of reaction of the Wijs reagent on fats and fatty acids but the reaction was too rapid to draw any positive conclusions with respect to the different components of the fatty acids.

Kaufmann⁴ describes the use of bromine instead of iodine for the analysis of oils and has shown the action of bromine in a number of solvents toward highly unsaturated compounds. Thus, bromine dissolved in carbon tetrachloride was found to be less reactive than bromine in chloroform and, further, bromine in methyl alcohol saturated with sodium bromide was in most cases less reactive than in carbon tetrachloride. The latter mixture he recommended as a reagent for the analysis of oils. Kaufmann also reported some data showing a comparison of the rate of bromination of linseed oil in carbon tetrachloride and in methyl alcohol saturated with sodium bromide. The experiments were carried out in sunlight and in the dark; the results are given as the equivalent of iodine absorbed. The results reported by Kaufmann are as follows.

TABLE I
BROMINATION OF LINSEED OIL (IODINE No. 182)

Time	Carbon tetrachloride		Methyl alcohol and sodium bromide	
	Dark	Sunlight	Dark	Sunlight
2 min.	152.0	178.1
10 min.	151.2	183.0	156.2	161.3
30 min.	152.8	190.5	157.4	163.8
60 min.	156.8	194.3	160.7	164.3
24 hours	183.0	239.5 ^a	183.3	182.0
48 hours	182.0	252.0	183.5	181.6

^a No mention is made by Kaufmann as to whether any substitution had taken place to give these high values.

Kaufmann⁵ also reported the rate of bromination of cinnamic acid both in the dark and in ultraviolet light but no mention is made of the use of ultraviolet light in the experiments with linseed oil. He reported the addition of six bromine atoms to elaeostearic acid and no substitution when exposed to ultraviolet light for forty minutes.

Coffey⁶ has shown that the different constituents of linseed oil oxidize differently, so that it would appear reasonable to assume that the different constituents should brominate differently.

³ Cerdeiras, *Bull. soc. chim.*, **35**, 902-904 (1924).

⁴ Kaufmann, *Z. Untersuch. Lebensm.*, **51**, 3 (1926).

⁵ Kaufmann, *Ber.*, **59**, 1390 (1926).

⁶ (a) Coffey, *J. Chem. Soc.*, **119**, 1408 (1921); (b) **28**, 286 (1925).

Experimental Procedure

These investigators have shown that unsaturated compounds react slowly with bromine when the solution is dilute. Sunlight and ultraviolet light increase this rate of reaction, producing greater bromine absorption without necessarily causing substitution.

In order to study the action of bromine on "drying" oils, the fatty acids of poppy seed, soya bean, linseed and perilla oils were treated with a dilute solution of bromine in carbon tetrachloride for different periods of time. The amount of bromine that reacted with the fatty acids was calculated on the basis of iodine numbers. The calculation to an iodine number was made so as to have a ready reference to the ordinary iodine number of the fatty acids as determined by the Wijs method. These results were then compared with the results for oleic, linolic and linolenic acids by similar treatment. In order to determine if light produced any action between bromine and the fatty acids aside from substitution, the fatty acids were allowed to stand in contact with bromine for an hour in the dark. These solutions were then subjected to ultraviolet irradiation for definite periods of time and the amounts of additive and substitutive bromine determined.

Materials

Bromine-Carbon Tetrachloride Solution.—Two and six-tenths cc. of bromine was added to 800 cc. of Eastman Kodak Co. "sulfur free" carbon tetrachloride which was freshly distilled over phosphorus pentoxide before adding the bromine. It is necessary that extreme precaution be taken to have the liquids dry or else bromine acids will form and cause substitution with the fatty acids.

Fatty Acids.—Twenty-five g. of poppy seed, soya bean, linseed and perilla oils were each dissolved in 50 cc. of alcohol and saponified with potassium hydroxide in an atmosphere of carbon dioxide. The potassium soaps were converted into the free acids by treatment with dilute hydrochloric acid. The fatty acids were then dissolved in ethyl ether and dried over anhydrous sodium sulfate. The ether was evaporated just before using the acids.

The fatty acids from the different oils had the following iodine numbers by the Wijs method.

Poppy seed oil fatty acids.....	135.5
Soya bean oil fatty acids.....	137.0
Linseed oil fatty acids.....	186.4
Perilla oil fatty acids.....	197.1

Oleic Acid.—The oleic acid used was so-called c. p. quality. It had an iodine number of 86.0. The theoretical iodine number is 90.

Linolic Acid.—The linolic acid was so-called c. p. quality with an iodine number of 184.0; theoretical, 181.4.

Linolenic Acid.—The linolenic acid was prepared by treating 50 g. of white crystalline hexabromostearic acid with 15 g. of freshly reduced zinc dust in 100 cc. of absolute methyl alcohol saturated with dry hydrogen chloride gas. This mixture was refluxed on a water-bath and mechanically stirred for about three hours. Dry carbon dioxide and hydrogen chloride was passed into the flask during the reaction. The mixture was then treated with warm brine to remove the methyl ester from excess methyl

alcohol. The methyl ester of linolenic acid was then saponified with potassium hydroxide and the potassium salt hydrolyzed with dilute hydrochloric acid. The linolenic acid thus produced was washed several times with water until it gave no test for halogens. It was then dissolved in ethyl ether to remove any unchanged hexabromide, filtered and the ethereal solution dried with sodium sulfate. The ether was removed by distillation; yield, 90%. This linolenic acid had an iodine number of 222.8; theoretical, 274.3.

Method

In studying the reaction between bromine and the fatty acids in the dark the methods of McIlhiney and of Kaufmann were combined with some slight modifications. One g. of the fatty acid from the freshly saponified oil was dissolved in 200 cc. of the bromine-carbon tetrachloride solution and diluted to 250 cc. with carbon tetrachloride. The mixture was thoroughly shaken and placed in the dark at room temperature. At periods of 5, 10, 20 and 30 minutes, 1 hour, 24 hours and 48 hours, 25 cc. of the solution was removed, 15 cc. of a 15% solution of potassium iodide and 100 cc. of water were added and it was titrated with standard sodium thiosulfate solution in the usual manner. When the end-point was reached, 5 cc. of a 2% solution of sodium iodate was added. If the blue starch-iodide color reappeared, the titration was continued to the end-point. The amount of sodium thiosulfate used for this second titration was doubled and calculated as the substitution value.

In studying the reaction between bromine and the fatty acids due to ultraviolet irradiation, the method used was similar to the above except that the solution of fatty acids and bromine remained mixed in the dark for one hour, then 25cc. portions were placed in quartz tubes and exposed to a Cooper-Hewitt quartz Uviarc at a distance of 30 cm. (12 inches) for periods of 5, 15, 30 and 60 minutes. The titrations for additive and substitutive bromine were similar to the above. By keeping the reacting mixture in the dark for an hour the amount of bromine absorbed was in nearly all cases practically equivalent to the ordinary iodine number. As the study of the reaction under ultraviolet irradiation was not to increase the speed of the reaction but rather to determine if any increase in bromine addition took place, it was advisable practically to complete the additive reaction before exposure. Under this condition any increase in iodine number will correspond to bromine which does not react with the fatty acids in the dark.

Experimental Results

As mentioned before, instead of reporting the results as the amount of bromine absorbed, the calculations are converted to the equivalent iodine number.

The results have been presented in the following tables. Table II comprises the results of the reaction between the fatty acids of poppy seed, soya bean, linseed and perilla oils with bromine in the dark for definite periods of time. Table III shows the results of the same fatty acids and bromine after standing in the dark for one hour and then being exposed to ultraviolet light for definite periods. Table IV gives the results for oleic, linolic and linolenic acids corresponding to Table II, and Table V corresponds to Table III with the same acids. The columns headed "Addit." are equivalent iodine numbers corresponding to the amount of additive bromine, and those headed "Subst." correspond to substitutive bromine.

It is interesting to note that the amount of substitution seems to corre-

spond to the amount of hydroxy acids present in linseed oil. If this assumption is correct, then hydroxy acids may be present in poppy seed and perilla oils.

The effect of the ultraviolet light seems to increase the energy of the reacting mixture so that more bromine is absorbed by the fatty acids than under normal conditions.

TABLE II
REACTIONS IN THE DARK

Time of reaction	Poppy seed acids I no., 135.5		Soya bean acids I no., 137.0		Linseed acids I no., 186.4		Perilla acids I no., 197.1	
	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.
5 min.	126.5	2.9	129.7	0.0	161.6	2.9	161.1	0.7
10 min.	126.5	4.4	129.7	.0	162.7	4.4	164.0	1.4
20 min.	127.1	4.4	131.0	.0	164.4	4.4	165.8	1.4
30 min.	124.0	8.8	131.0	.0	165.1	4.4	171.0	2.9
1 hour	124.7	7.5	131.6	.0	166.2	4.4	184.5	4.4
24 hours	127.2	8.8	134.0	.0	174.4	4.4	191.4	8.4
48 hours	128.4	8.8	134.4	.0	176.3	5.1	195.4	8.8

TABLE III
REACTION IN THE DARK FOR ONE HOUR; THEN EXPOSED TO ULTRAVIOLET LIGHT

Time of reaction	Poppy seed acids I no., 135.5		Soya bean acids I no., 137.0		Linseed acids I no., 186.4		Perilla acids I no., 197.1	
	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.
5 min.	140.8	7.5	142.0	0.0	185.0	4.9	193.7	7.4
15 min.	151.0	8.8	144.7	.0	198.2	4.9	206.6	7.4
30 min.	167.1	10.3	151.3	.0	204.1	7.8	218.2	7.4
1 hour	166.3	12.6	161.0	.0	210.3	17.5	224.7	7.4

TABLE IV
REACTIONS IN THE DARK

Time of reaction	Oleic acid I no., 86.0		Linolic acid I no., 184.0		Linolenic acid I no., 222.8	
	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.
5 min.	89.5	0.0	177.8	0.0	209.8	0.0
10 min.	89.5	.0	179.5	0.0	209.0	.0
20 min.	90.3	.0	181.0	.0	210.9	.0
30 min.	90.7	.0	184.5	.0	214.4	1.2
1 hour	185.2	.0	214.4	1.2
24 hours	201.0	3.4	221.4	2.1

TABLE V
REACTION IN THE DARK FOR ONE HOUR; THEN EXPOSED TO ULTRAVIOLET LIGHT

Time of reaction	Oleic acid I no., 86.0		Linolic acid I no., 184.0		Linolenic acid I no., 222.8	
	Addit.	Subst.	Addit.	Subst.	Addit.	Subst.
5 min.	102.2	0.0	202.5	0.0	218.0	1.5
15 min.	102.5	.0	206.0	.0	220.0	3.7
30 min.	103.9	.0	222.1	.0	242.6	4.9

Discussion of Results

An examination of the results which are summarized in the tables indicates that in the case of the so-called pure oleic and linolic acids, there are

other substances present which react with bromine under the influence of ultraviolet light to yield the high values reported. The oleic acid used was the U. S. P. grade and might possibly contain some linolic acid. Likewise, linolic acid, which is usually prepared from poppy seed or soya bean oil, is also difficult to obtain pure. In fact, Pfahler⁷ claims that up to the present time pure linolic acid has not been prepared from an oil in a way analogous to Erdmann's method for linolenic acid. The high results with linolic acid may, therefore, be due partly to the presence of a stereo-isomer of linolenic acid which is not detectable by the hexabromide method of Eibner.

In the case of linolenic acid, which was prepared from hexabromolinolenic acid by de-bromination, according to the method of Erdmann, an iodine number lower than the theoretical is shown. Pfahler⁷ also states that the iodine number of acids prepared in this manner is always lower than the theoretical and that the low value is not due to impure acid. It is known that de-bromination in many cases causes stereomutation to forms which do not readily absorb halogen.

If this view is correct, then the acids should absorb more bromine under the influence of ultraviolet light. This has actually been accomplished, as will be seen from the results as given in tabular form. The abnormally high results for oleic and linolic acids beyond that assumed for the presence of other acids are as yet unexplainable, and work has been outlined, and is in progress, in an endeavor to explain these values. Linolenic acid, however, does not reach the theoretical value of absorption, even under the influence of ultraviolet light. It does show greater absorption than by the ordinary method, which indicates the presence of stereo-isomers.

The rate of bromine addition, in the dark, shows that oleic and linolic acids react more rapidly than linolenic acid. Oleic and linolic acids, therefore, should react more slowly toward oxygen than does linolenic acid, since compounds of this order which react slowly toward bromine do react more readily toward oxygen or hydroxyl. This is actually the case.

The results obtained on the mixed fatty acids of the different oils follow in a general way the results on the individual acids, with the further interesting observation that they all absorb more bromine under the influence of ultraviolet light than in the dark. This then indicated the presence of stereo-isomers which are not determined by present methods of analysis.

This same condition holds true for the other oils which are known to yield solid hexabromides under the ordinary treatment. The additional bromine absorbed means that, just as in poppy seed oil, there is another isomer present which does not react with bromine in the ordinary way.

⁷ Pfahler, *Chem. Umschau*, 33, 65-70 (1926).

The actual percentage of these isomers which are inactive toward bromine is approximately 10 to 15% in excess of the usual amount. In some cases the percentage may be lower than this. It is perhaps fortunate that these values are not high, because such substances in oils would be very energetic toward oxygen and thus cause too rapid drying of the oil.

Further evidence to support the authors' view of the presence of stereoisomers in linseed oil is the following.

Through the courtesy of H. A. Nelson and G. F. A. Stutz of the New Jersey Zinc Company, a sample of raw linseed oil was exposed to ultraviolet light in the presence of a dry carbon dioxide atmosphere for eighteen hours. This sample after exposure showed an iodine number of 148 and a hexabromide number of 35. This confirms the work of G. F. A. Stutz,⁸ who has shown a marked decrease in the iodine number of raw linseed oil after exposure to ultraviolet light in the presence of nitrogen gas.

However, when this sample of oil was brominated in the presence of ultraviolet light for thirty minutes, the total bromine absorbed was equivalent to an iodine number of 190, as against 180 for the original raw, unexposed oil.

In the first exposure of the raw oil in the presence of carbon dioxide, the ultraviolet rays caused a mutation of the stable isomers to labile isomers. This is in accordance with the views of Stoermer⁹ and others.

In the second exposure, where the pre-exposed oil was brominated, the action of the ultraviolet rays stimulates the addition of halogen to the isomers which were stereomuted in the first exposure. It is known that labile isomers react very slowly with halogen and, furthermore, they react easily with oxygen. This too was found to be the case, for the oil from the first exposure (iodine No. 148) dried more rapidly than the raw, unexposed oil.

It is apparent, therefore, that the ultraviolet rays in thirty minutes' time could hardly have changed the labile form to that which required eighteen hours to accomplish in the other direction, but that they simply stimulated the absorption of the halogen.

Our experiments so far indicate that the optimum condition for bromination under the influence of ultraviolet light is attained just at the point where substitution begins. A small substitution value is discernible in practically all glycerides which represents hydroxy acids, even before exposure, so that this value must be considered first before assuming substitution by ultraviolet light.

Conclusions

The rate of bromination of oleic, linolic and linolenic acids is in inverse ratio to the number of double bonds, that is, oleic acid reacts the most rapidly and linolenic acid the least.

⁸ Stutz, *Ind. Eng. Chem.*, **18**, 1238 (1926).

⁹ Stoermer, *Ann.*, **342**, 1 (1905).

The rate of bromination of the mixed fatty acids of poppy seed, soya bean, linseed and perilla oils is in direct relation to the acid constituents.

Under the influence of ultraviolet light the bromination of both the so-called pure acids and the mixed fatty acids proceeds beyond the bromination in the dark, which indicates the presence of unsaturated isomers which are not shown by present methods of analysis.

BETHLEHEM, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE] .

THE CONSTITUTION OF ORTHO-NITROBENZALDEHYDE AND THE INTERFERENCE OF NITRO AND NITROSO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

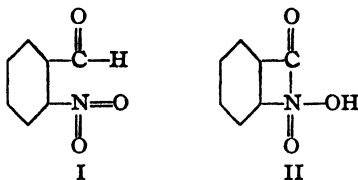
BY HENRY GILMAN AND ROBERT E. FOTHERGILL¹

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Introduction

In connection with a study of the mechanism of the photochemical reactions of *o*-nitrobenzaldehyde and some of its condensation products, Tanasescu² has suggested recently that *o*-nitrobenzaldehyde is very probably an equilibrium mixture of the following forms:



The chief evidence brought forward in support of the cyclic hydroxy formula (II) is the quantity of methane evolved when *o*-nitrobenzaldehyde is treated with methylmagnesium iodide according to the method of Zerewitinoff.³ This quantitative method for the estimation of active hydrogens has been used very extensively and, on the whole, is eminently satisfactory.

However, Tanasescu is probably quite wrong in suggesting that *o*-nitrobenzaldehyde has the cyclic hydroxy formula (II) because the compound evolves methane when treated with methylmagnesium iodide. We do not say that a formula like (II) is impossible. If it is a likely formula it must find support in evidence other than that given by the Zerewiti-

¹ A preliminary report on this work was presented at Iowa City, May 7, 1927, before the Organic Division of the Iowa Academy of Science.

² Tanasescu, *Bull. soc. chim.*, 39, 1443 (1926).

³ Zerewitinoff, *Ber.*, 40, 2023 (1907), and numerous succeeding papers. The most recent reference is the *Z. anal. Chem.*, 68, 321-327 (1926) [*C. A.*, 21, 153 (1927)]. See also Chugaev, *Ber.*, 35, 3912 (1902), for earlier experimental work on the same method.

noff method. The present quantitative studies on the gases evolved show that the phenomenon of gas evolution is essentially an inherent property of the nitro and nitroso groups.

Tanasescu used methylmagnesium iodide in his studies and, as well as can be ascertained from his data, the gas evolved was merely measured and not analyzed to ascertain whether it was pure methane or a mixture of hydrocarbons. Such analyses have been carried out in our work and although the gas evolved when methylmagnesium iodide is used is largely methane, as one would expect if any hydroxyl group were present, the same is not true with other alkylmagnesium halides like the ethyl-, propyl- and butylmagnesium bromides. With these other alkylmagnesium halides varying amounts of unsaturated and R. R. hydrocarbons are evolved in addition to ethane, propane and butane.

Experimental

All of the experiments were carried out under the standard conditions of earlier workers. A few of the compounds were studied in *n*-butyl ether according to Zerevitinoff's⁴ technique. Most of the determinations, however, were made by the revised method of Moureu and Mignonac,⁴ in which ethyl ether is used as the medium. Ciusa⁵ also used the technique of Moureu and Mignonac. Blank runs with pure benzoic acid were made in both methods in order to assure ourselves of correct manipulation.

The compounds used were of the highest purity commercially available and in a few cases additional special purification processes were used.

The gases evolved were analyzed by standard methods of combustion, preceded by removal of ether, unsaturated hydrocarbons and oxygen.

An experiment with nitrobenzene and methylmagnesium iodide in *n*-butyl ether showed that most of the gas was evolved at room temperature during the first ten minutes.⁶ However, in order to displace any dissolved gas and to expedite the several determinations, the reaction flask was immersed in a beaker of water at 60–70°. It was allowed to stand under these conditions for fifteen minutes, after external heat was removed. At the end of this period the water-bath was removed, the flask cooled to room temperature and a reading was then made of the volume of gas evolved.

The analysis of the saturated gas by the explosion method followed by measurement of carbon dioxide and water showed that the quantity of saturated hydrocarbon that might have been formed by a coupling reaction (for example, ethane when methylmagnesium iodide was used) was generally quite small and did not exceed several per cent. In order to verify this, two large runs were made with *n*-butylmagnesium bromide and cyclohexylmagnesium bromide. Forty-nine and two-tenths g. (0.4 mole) of nitrobenzene dissolved in 100 cc. of dry ether was added slowly to 2.25 moles of *n*-butylmagnesium bromide—an amount which was sufficient to give a positive color test for RMgX compound. After hydrolysis, careful fractionation gave about 2 g. (1.6%)

⁴ Moureu and Mignonac, *Compt. rend.*, **158**, 1624 (1914).

⁵ Ciusa, *Gazz. chim. ital.*, **50**, II, 53 (1920); *C. A.*, **15**, 837 (1921).

⁶ About 0.8 active hydrogen equivalent of gas was evolved during the first ten minutes. At the end of two hours, the equivalent of active hydrogen increased to 0.99. Finally, in this particular experiment, heating for fifteen minutes at 60–70° increased the active hydrogen equivalent to 1.35. This particular determination was the last of those made in the present study.

of *n*-octane and 6.0 g. or 3.6% of *n*-butyl alcohol. The reaction mixture of 0.17 mole of nitrobenzene and 0.4 mole of cyclohexylmagnesium bromide gave 2.4 g. or 3.6% of di-cyclohexyl.

TABLE I
RESULTS

No.	Compound	G. of compound	Grignard reagent	Gas evolved, (Cc stand. cond.)	No. of active hydrogens
1	Benzoic acid	0.2034	CH ₃ MgI	33.2	0.89
		.2063		36.6	.96
		.2076		37.2	1.03 ^a
2	Nitrobenzene	.2876	CH ₃ MgI	51.2	0.98
		.2214		41.7	1.03
		.1993		34.4	0.95
		.4849		87.2	.99
3	Benzoic acid	.5206	C ₂ H ₅ MgBr	96.5	1.01 ^b
4	Nitrobenzene	.6004	C ₂ H ₅ MgBr	170.8	1.56
		.5724		155.7	1.50
5	<i>o</i> -Nitrotoluene	.6871	C ₂ H ₅ MgBr	180.0	1.60
		.3412		98.7	1.77 ^c
6	<i>p</i> -Nitrotoluene	.5872	C ₂ H ₅ MgBr	158.5	1.65 ^d
7	1,3,5-Trinitrobenzene	.1992	C ₂ H ₅ MgBr	31.2	1.49 ^e
8	<i>o</i> -Nitrobenzaldehyde	.5007	C ₂ H ₅ MgBr	121.9	1.65 ^f
		.5005		124.9	1.68
9	<i>m</i> -Nitrobenzaldehyde	.5297	C ₂ H ₅ MgBr	112.0	1.43 ^g
10	Nitrosobenzene	.4020	C ₂ H ₅ MgBr	91.8	1.09 ^h
11	<i>p</i> -Nitrosodiethylaniline	.5012	C ₂ H ₅ MgBr	46.4	0.74 ^h
12	Nitrobenzene	.6184	<i>n</i> -C ₄ H ₉ MgBr	213.8	1.90 ⁱ
13	Nitrobenzene	.7228	<i>n</i> -C ₄ H ₉ MgBr	221.6	1.68 ⁱ

^a When carried out at room temperature the number of active hydrogen was 0.98. However, when the reaction flask was heated to from 60–70° for fifteen minutes, then cooled and the gas measured, the number was 1.03. This slight increase was undoubtedly due to the expulsion of some dissolved gas. Accordingly, all other experiments with *n*-butyl ether were heated in like manner. With ethyl ether as the solvent the temperature of the water-bath was 40–45°.

^b This gas contained 0.5% of unsaturated compounds. Very probably this is due to a small quantity of ethylene formed in the preparation of ethylmagnesium bromide.

^c Included in this gas was 13% of unsaturated compounds.

^d There was 16.5% of unsaturation in this gas.

^e This includes 5.9% of unsaturation.

^f This includes 10.5% of unsaturation, and the other run giving 1.68 active hydrogen showed 8.0% unsaturation. The authors wish to thank the Eastman Kodak Company for the sample of *o*-nitrobenzaldehyde used in this study.

^g This includes 12.2% of unsaturation.

^h Includes 12.6% unsaturation, whereas the *p*-nitrosodiethylaniline has 9.6% unsaturation.

ⁱ Includes 10.8% unsaturation, whereas the experiment with *n*-butylmagnesium bromide gave 12.9% unsaturation.

Discussion of Results

The results in Table I show that all the nitro and nitroso compounds studied evolve varying amounts of gas when treated with alkylmagnesium

halides having an alkyl group of low molecular weight. In a way it is largely fortuitous that nitrobenzene shows but one active hydrogen when treated with methylmagnesium iodide;⁶ for, had ethylmagnesium bromide been used—a reagent which in the hands of others⁴ has given good results in estimating active hydrogen in a miscellany of compounds—the number of active hydrogens would have been about 50% greater. In this connection it is to be noted that *n*-propyl- and *n*-butylmagnesium bromides also give higher results than those obtained with methylmagnesium iodide.

The gas evolved from the two nitrobenzaldehydes studied is probably independent of the aldehyde group present, because benzaldehyde under corresponding conditions evolves no gas.

Tanasescu² got about one active hydrogen equivalent with *o*-nitrobenzaldehyde and less than one-third of an active hydrogen with *p*-nitrobenzaldehyde. He used methylmagnesium iodide, but on the basis of our results with different alkylmagnesium halides it is obvious that had he used a higher alkylmagnesium halide he would have found more active hydrogen. In this way he might have avoided the error of advancing formula (II), which is postulated as having one hydroxyl group largely because it evolves one equivalent of gas with methylmagnesium iodide.

Summary

The cyclic hydroxy structure proposed for *o*-nitrobenzaldehyde has no support on the basis of gas evolved when treated with an alkylmagnesium halide of low molecular weight. Gas evolution has been shown to be an inherent property of nitro and nitroso groups, and the Zerewitinoff method cannot be used with substituted aromatic nitro and nitroso compounds unless corrections are made for the gas evolved because of the nitro or nitroso group.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYME NE STUDIES. VIII. A. PARA-CYMYLENE-2,5-DIAMINE. B. NEW DYES DERIVED FROM 2-AMINO- AND 2-AMINO-5-BROMO-*p*-CYME NE

BY ALVIN S. WHEELER AND LILLIE F. P. CUTLAR¹

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In order to obtain cymylene-2,5-diamine we first acetylated 2-aminocymene (an Eastman Kodak product) but in view of the difficulty encountered in purifying the acetate we examined the statement of Wallach and Schrader² that a di-acetyl derivative, melting at 66°, may be prepared. We carried out six experiments, as follows: (1) boiled one mole of aminocymene (A) with one mole of acetic anhydride (B); (2) boiled A with a large excess of B; (3) one mole of A with one mole of acetyl chloride (C) in ether; (4) one mole of A with two moles of C in ether; (5) two moles of A with one mole of C in ether; (6) A with large excess of C in ether. In all cases the mono-acetyl compound, melting at 71°, was obtained. Our own method was to treat an acetone solution of aminocymene with a large excess of acetyl chloride, pouring the mixture into a large quantity of water. The acetate was nitrated as described by Andrews,³ modifying the process by pouring the nitration mixture into a sodium hydroxide solution containing ice. Even so the product was purified with difficulty. Its acetone solution was boiled many times with kelp char before the product could be recrystallized from alcohol. The nearly white needles melted at 168°. The location of the nitro group was proved by converting it into di-acetylcymylene-2,5-diamine prepared by Kehrmann and Messinger⁴ and by Wallach,⁵ these authors giving 260° as the melting point. The usual reducing agents failed to give a product which could be purified, but success was obtained with titanium trichloride and hydrochloric acid in an atmosphere of carbon dioxide, with the assistance of H. A. Ljung in this Laboratory. The desired compound, melting at 260°, was obtained on acetylating the reduction product with acetic anhydride and sodium acetate. Kehrmann and Messinger obtained it from thymoquinonedioxime. We then obtained this diacetate by a very different method. Aminocymene was coupled with diazotized sulfanilic acid. The dye produced was reduced with stannous chloride and the diamine ob-

¹ This paper is an abstract of a thesis submitted by Lillie F. P. Cutlar in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina, in June, 1927.

² Wallach and Schrader, *Ann.*, 279, 375 (1893).

³ Andrews, *J. Ind. Eng. Chem.*, 10, 453 (1918).

⁴ Kehrmann and Messinger, *Ber.*, 23, 3562 (1890).

⁵ Wallach, *Ann.*, 336, 23 (1904).

tained was acetylated. This method also indicates that the second amino group is in position 5 and also the nitro group because the coupling must take place in a position para to the amino group.

Three new salts of aminocymene were prepared: the nitrate, the hydrobromide and the trichloro-acetate. Two new dyes were prepared by coupling aminocymene with sulfanilic acid and with *p*-nitrosodimethylaniline, the latter dye being of the Eurhodine type. The sulfanilic acid dye furnishes a splendid raw material for the preparation of cymylene-2,5-diamine.

The bromination of aminocymene was first carried out by the method used by one of us and Smithey⁶ in which a carbon tetrachloride solution of aceto-amidocymene is treated with bromine, the product then being hydrolyzed. But since the hydrobromide of aminobromocymene was needed for most of the work, the acetylation step was omitted and the aminocymene directly brominated. Apparently the only product of the reaction was the hydrobromide of 2-amino-5-bromo-*p*-cymene. It will be recalled that Kekulé⁷ brominated aniline directly and obtained a bad mixture of aniline hydrobromide, monobromo-, dibromo- and tribromo-aniline. As two more hydrogen are substituted in aminocymene than in aniline we have a very different situation. Azo dyes were obtained by coupling aminobromocymene with *o*-cresol, catechol, phloroglucinol, carvacrol and *p*-toluidine. In addition sulfanilic acid and anthranilic acid were diazotized and coupled with aminobromocymene.

Their color reactions with sulfuric acid were noted. The names given to the colors are based on Ridgway's Standards.⁸

Experimental Part

Salts of 2-Amino-*p*-cymene

The three salts described below were made by mixing the constituents in the cold. They were recrystallized from a mixture of ether and petroleum ether. All are soluble in water, alcohol, acetone and ether and melt with decomposition. Analysis was made by titration with potassium hydroxide, using methyl red as indicator

Compound	Crystals	M. p., °C.	Subs., g.	0.1095 <i>N</i> KOH, cc.	Analysis, acid calcd., %	found, %
Nitrate	Plates	140	0.5248	22.71	31.47	31.66
Hydrobromide	Needles	169	.2066	8.32	35.14	35.49
Trichloroacetate	Plates	162	.3282	11.55	52.27	52.52

Dyes Derived from 2-Amino-*p*-cymene

5-(4-Sulfobenzene-azo)-carvacrylamine Hydrochloride, $C_{16}H_{16}O_2N_2ClS$.—Ten g. of sulfanilic acid was diazotized and added to a solution of 7.5 g. of aminocymene suspended in 50 cc. of water containing 10 cc. of concd. hydrochloric acid. The red precipi-

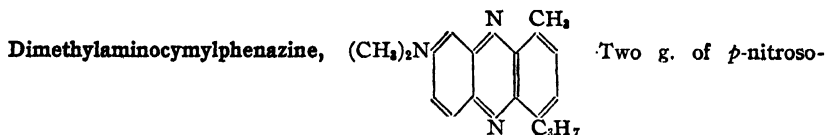
⁶ Wheeler and Smithey, *THIS JOURNAL*, **43**, 2611 (1921).

⁷ Kekulé, *Zeit. für Chem.*, **9**, 687 (1866).

⁸ Ridgway "Color Standards and Color Nomenclature," Washington, D. C., 1912.

tate was recrystallized from methyl alcohol, giving Nopal red needles melting at 282°. It gives a cherry red color with dil. sulfuric acid, red brown with the concd. acid, becoming ruby red when heated.

Anal. Subs., 0.2513: AgCl, 0.0938. Calcd. for $C_{16}H_{20}O_4N_2ClS$: Cl, 9.58. Found: 9.24.



dimethylaniline was dissolved in hot methyl alcohol and to the solution was added 2.0 g. of aminocymene. The solution was boiled and the alcohol evaporated off, the residue being taken up with water. On standing, crystals separated which on recrystallizing from boiling water formed deep slate-blue needles, melting with decomposition at 48°. The dye is soluble in acetone and alcohol. Alkaline hydrosulfite reduces it to a colorless compound which is oxidized back to its original color with sodium perbromate. It belongs to the Eurhodine group of dyes. In dilute sulfuric acid it gives a red-green fluorescence, a dark brown color with the concd. acid and no change when heated.

Anal. Subs., 0.2722: 19.45 cc. of 0.1515 *N* HCl required for NH_3 . Calcd. for $C_{18}H_{21}N_3$: N, 15.04. Found: 14.84.

Derivatives of 2-Amino-5-bromo-*p*-cymene

Sulfate, $CH_3C_6H_7BrC_6H_4H_2SO_4$.—Aceto-amidobromocymene was refluxed with an excess of 50% sulfuric acid until solution took place. The crystals which separated on cooling were recrystallized from dilute alcohol. If recrystallized from sulfuric acid they remained wet; shining white needles, melting with decomposition at 123°.

Anal. Subs., 0.1964: 10.93 cc. of 0.1095 *N* KOH. Calcd. for $C_{10}H_{10}O_4NBrS$: H_2SO_4 , 30.08. Found: 29.62.

New Azo Dyes

These dyes were prepared by diazotizing the aminobromocymene at 0°, adding the phenol dissolved in alkali, precipitating the dye with acid and recrystallizing the dye from a suitable solvent.

TABLE I
PREPARATION

No.	Name ^a	Formula	Coupler	Solvent
1	5-(5-Bromocarvacrylazo)-2-cresol	$C_{17}H_{19}ON_2Br$	<i>o</i> -Cresol	Alcohol
2	5-(5-Bromocarvacrylazo)-catechol	$C_{16}H_{17}O_2N_2Br$	Catechol	Toluene
3	2-(5-Bromocarvacrylazo)-1,3,5-trihydroxybenzene	$C_{18}H_{17}O_4N_2Br$	Phloroglucinol	Alcohol
4	5-(5-Bromocarvacrylazo)-carvacrol	$C_{18}H_{20}ON_2Br$	Carvacrol	Alcohol
5	3-(5-Bromocarvacrylazo)-4-aminotoluene hydrochloride	$C_{17}H_{21}N_2BrCl$	Toluidine	Methyl alc.
6	8-(4-Sulfobenzene-azo)-5-bromocarvacrylamine hydrochloride	$C_{18}H_{19}O_2N_2BrCl$	Sulfanilic acid ^b	Chloroform
7	3-(2-Carboxylbenzene-azo)-5-bromo-carvacrylamine hydrochloride	$C_{18}H_{19}N_2BrCl$	Anthranilic acid ^b	Methyl alc.

^a Based on analogy.

^b These acids were diazotized and coupled with aminobromocymene.

TABLE II
PROPERTIES

No.	Color	M. p., °C.	Behavior with concd. H ₂ SO ₄			Analyses			
			Cold	Hot	Dilute	Weight Subs.	Ag hal.	Percentage halogen Calcd.	Found
1	Chestnut-brown	112	Red-brown	Dark brown	Pale straw	0.1856	0.0972	22.96	22.38
2	Buffy-brown	235	Red-brown	Deep brown	Pale straw	.3916	.2238	24.21	24.22
3	Morocco-red	280	Red-purple	Deep purple	Pale pink	.1696	.0882	21.88	21.52
4	Liver-brown	192	Garnet	Dark red	Insol.	.2130	.1263	20.01	20.48
5	Mikado-brown	188	Ruby-red	Deep red	Straw	.2208	.1679 ^a	31.46	31.09
6	Deep chrome	+300 ^b	Dull brown	Dark brown	Light orange	.2374	.1460 ^a	25.71	25.62
7	Diamine brown	189	Deep purple	Deep red	Red-purple	.3162	.2512 ^a	32.62	32.48

^a AgCl + AgBr.
^b Decomp.

Summary

1. The nitrate, hydrobromide and trichloro-acetate of 2-amino-*p*-cymene were prepared.
2. Aminocymene gave dyes with sulfanilic acid and with *p*-nitrosodimethylaniline, the latter being a Eurhodine.
3. The sulfanilic acid dye is an excellent raw material for making cymylene-2,5-diamine.
4. The sulfate of 2-amino-5-bromo-*p*-cymene was prepared.
5. New azo dyes were prepared by coupling 2-amino-5-bromo-5-cymene with *o*-cresol, catechol, phloroglucinol, carvacrol and *p*-toluidine. Sulfanilic and anthranilic acids were diazotized and coupled with aminobromocymene.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM LABORATORIES OF THE NEW YORK STATE COLLEGE OF FORESTRY
AND THE CHEMICAL DEPARTMENT OF SYRACUSE UNIVERSITY]A NOTE CONCERNING A NEW METHOD FOR THE PRODUCTION
OF CELLOBIOSE FROM CELLOBIOSE OCTA-ACETATE

BY F. C. PETERSON AND C. C. SPENCER

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PUBLISHED NOVEMBER 5, 1927

Cellobiose (or cellulose as it was formerly called) is a disaccharide sugar obtained by partial hydrolysis or acetolysis of either cotton or wood cellulose. It is also the product of the action of certain microorganisms on cellulose.

Cellobiose is at present attracting considerable interest in the field of bacteriology. It has been found that cellobiose may be used as a test for the separation of two types of bacteria commonly found in water. Previously the identification of these two types of organisms has been the result of data compiled from correlated tests. Cellobiose, however, is utilized by *A. aerogenes* with acid and gas formation, whereas no changes

are brought about by any strains of *B. coli*. This test is, therefore, specific in differentiating these two types of organisms. When applied to public health work it may thus be used to indicate the presence or absence of fecal pollution.

The literature at present reveals two procedures for the preparation of this sugar. The method given by Skraup and König¹ and published in 1899 is the older of the two, and the second, described by Maquenne and Goodwin² and published in 1904, is really a modification of the former method. Both of them depend on the saponification of the octa-acetate of the sugar by means of alcoholic potassium hydroxide, with subsequent isolation of the sugar from the potassium salt by means of an acid (aqueous acetic acid was used by Skraup and König; perchloric acid was used by Maquenne and Goodwin). In either case the solutions after acid treatment were concentrated *in vacuo* to a sirup or solid and the sugar was purified by repeated crystallization from methanol or ethanol.

Experiments in our Laboratories have shown that either of the methods gives satisfactory yields in the preparation of this sugar. Yield figures of purified cellobiose up to 75% were obtained. The procedures involved are, however, long and tedious and cellobiose if prepared commercially in this manner would necessarily have to be quoted at \$3.00 or \$4.00 per gram. In order that the time factor might be reduced and the yield increased, if possible, other means of preparation were sought.

A procedure has been developed which reduces the time of preparation to approximately one-half that formerly required and yields up to 85% of purified cellobiose have been obtained. Quantitative studies of the method have been confined to the preparation of several batches of this sugar.

The procedure for the newly developed method was as follows.

A 10% solution of sodium ethylate was prepared in 95% alcohol. Ten grams of finely pulverized cellobiose octa-acetate were incorporated into 85 cc. of this solution during a period of one hour. The mixture was constantly agitated by a mechanical stirrer. The reaction took place rapidly, as evidenced by the strong odor of ethyl acetate which was given off almost immediately after the addition of the first portions of the acetate, and was complete in less than one hour. The time limit of one hour was allowed in order that any small lumps of the acetate (resulting from improper pulverization) might be completely saponified. The sodium salt was then collected by filtration, washed with absolute alcohol and dissolved in a minimum volume of water and again filtered. To the resulting aqueous solution glacial acetic acid was slowly added until a precipitate began to form.

Very frequently complete crystallization of the cellobiose took place

¹ Skraup and König, *Monatsh.*, 22, 1011 (1901).

² Maquenne and Goodwin, *Bull. soc. chim.*, 31, 854 (1904).

within 10 or 15 minutes after the addition of sufficient glacial acetic acid. In other cases it was necessary to allow the mixture to stand overnight in order that complete crystallization might be effected. Apparently somewhat decreased yields result when it becomes necessary to adopt the latter procedure.

The crude cellobiose was collected by filtration, washed with ether and dried at 65°. Purification of the crude sugar was accomplished by dissolving it in a minimum volume of water, filtering and adding acetone to the aqueous solution until reprecipitation was complete. A product of sufficient purity was usually obtained after two such recrystallizations from acetone. Approximately 80% of the acetone was recoverable by fractional distillation. Yields of crude cellobiose as high as 95% have been obtained by the use of this method. Yields of purified sugar as high as 85% have also been obtained. The purified sugar melted at 225° (uncorr.) and gave satisfactory results when analyzed for carbon and hydrogen. Its rotation (in water) was 24.4° at the end of fifteen minutes and 35.2° at the end of 27 hours.

The advantages derived through the use of this method over those previously employed for the preparation of cellobiose from its acetate are as follows:

(1) Yield figures of both crude and purified cellobiose are materially higher than those by the methods of Skraup and König and Maquenne and Goodwin. The yield of purified sugar melting at 225° (uncorr.) has been increased approximately 10%.

(2) The crude cellobiose as it crystallizes from glacial acetic acid is free from any gummy, foreign material. When using the methods employed by the former investigators some gummy material is always associated with the crude cellobiose. Contamination of the crude sugar by this gum increases the number of recrystallizations necessary in order that a product of sufficient purity may be obtained. Inasmuch as each recrystallization is accompanied by a decrease in yield and inasmuch as the number of recrystallizations is less by the use of our method than by those previously employed, this may explain in part the higher yields which we were able to obtain.

(3) The time consumed in the preparation of cellobiose is reduced approximately one-half and in some cases three-quarters of that formerly required.

(4) Needle-shaped crystals of purified cellobiose measuring approximately two millimeters or over in length are consistently obtained. Upon only one occasion during a period of two years have crystals of this size been obtained when following the methods of Skraup and König or Maquenne and Goodwin. These latter methods usually yield needle-shaped crystals of approximately $\frac{1}{10}$ of one millimeter in length.

(5) Both labor and cost of materials are reduced. This allows cellobiose to be prepared commercially at a figure which is not prohibitive to those laboratories desiring to use it in public health work.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

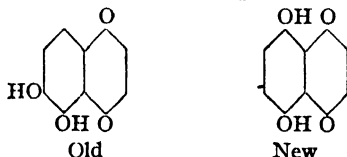
HYDROXYNAPHTHOQUINONE STUDIES. VII. THE BROMINATION OF NAPHTHAZARIN

BY ALVIN S. WHEELER AND B. G. CARSON¹

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The first study of the bromination of naphthazarin was carried out by one of us and Edwards.² The constitution of naphthazarin was regarded at that time as 5,6-dihydroxy-1,4-naphthoquinone but it has now been proved to be 5,8-dihydroxy-1,4-naphthoquinone. Dimroth and Ruck³



have shown that pyroboro-acetate reacts with naphthazarin to form a di-boro-acetate. Therefore, the two hydroxyl groups must be para to each other and not ortho, since this reaction occurs between carbonyl and hydroxyl groups ortho to each other. Pfeiffer⁴ has shown that tin tetrachloride forms an addition product with loss of one molecule of hydrochloric acid, such a reaction occurring with hydroxyquinones where the carbonyl is ortho to the hydroxyl group. Many formulas in the literature are now affected by this new formula for naphthazarin.

Bromination of Naphthazarin

Naphthazarin takes up a maximum of four atoms of bromine in hot glacial acetic acid solution. Positions 2, 3, 6 and 7 are undoubtedly occupied (Formula II). This tetrabromo naphthazarin gives a diacetyl derivative (III) and a dianilide (IV) on boiling with aniline. In the latter reaction the aniline may have reacted with the bromine atoms of the quinone ring or with those of the phenol ring. The same doubt exists in regard to the relative mobility of the hydrogen atoms of the two rings in naphthazarin. When two chlorine or bromine atoms are taken up, which ring do

¹ This paper is an abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at the University of North Carolina, in June, 1927.

² Wheeler and Edwards, *THIS JOURNAL*, 39, 2460 (1917).

³ Dimroth and Ruck, *Ann.*, 446, 123 (1926).

⁴ Pfeiffer, *Ber.*, 60, 111 (1927).

⁷ Zincke and Schmidt, *Ann.*, 286, 41 (1895).

Experimental Part

2,3,6,7-Tetrabromonaphthazarin (II).—Five g. (1 mole) of pure sublimed naphthazarin was dissolved in 139 cc. of glacial acetic acid and treated with 15.9 g. of bromine (a little less than four moles). The mixture was boiled under a reflux for eight hours. The product separated on cooling the solution. It was recrystallized from glacial acetic acid, using 35–45 cc. of acid for each gram of product. The crystals are slender, flat, bronze-colored needles, melting at 300°. The compound is insoluble in ether, difficultly soluble in hot alcohol and acetone but easily soluble in hot chloroform, carbon tetrachloride and glacial acetic acid. It is very soluble in toluene. This derivative may also be prepared by allowing the brominating mixture to stand for three weeks at room temperature.

Anal. Subs., 0.1195: AgBr, 0.1772. Calcd. for $C_{10}H_4O_4Br_4$: Br, 63.24. Found: 63.11.

Acetylation yields a diacetate and aniline a dianilide derivative. The bromine is removed by boiling the compound with a 2% hydrochloric acid solution of stannous chloride.

Diacetate (III).—The diacetate was best prepared by first making the sodium salt of the tetrabromonaphthazarin by the ether-sodium carbonate method and then treating the salt with a mixture of equal parts of acetyl chloride and acetic anhydride. Enough of the liquid mixture was used to act as a solvent. It was heated until no further change took place in color, which passed from blood-red to yellow. The product was precipitated with water. It is easily soluble in glacial acetic acid, acetone, chloroform and benzene but difficultly soluble in alcohol and ether. It is best recrystallized from boiling chloroform. It forms light yellow, granular crystals, melting at 262°. It can also be prepared from tetrabromodiquinone by simultaneous reduction and acetylation.

Anal. Subs., 0.1714: AgBr, 0.2185. Calcd. for $C_{10}H_6O_6Br_4$: Br, 54.24. Found: 54.25.

Dianilide (IV).—Two g. (1 mole) of tetrabromonaphthazarin was dissolved in 250 cc. of alcohol and 1 g. of aniline added. The mixture was refluxed for eight hours when, judging from the color of the solution, the reaction was complete. The solution was concentrated to 25 cc. and cooled. The product was recrystallized three times from glacial acetic acid. It consisted of microscopic bronze-colored needles, melting at 251°. There were some red fumes about twenty degrees below the melting point; weight, 2.3 g. It is easily soluble in benzene, alcohol and glacial acetic acid. It dissolves in sodium carbonate solution.

Anal. Subs., 0.1626: AgBr, 0.1200. Calcd. for $C_{22}H_{14}O_4N_2Br_2$: Br, 31.83. Found: 31.41.

2,3,6,7-Tetrabromodiquinone (V).—Five g. of naphthazarin was dissolved in 150 cc. of glacial acetic acid and treated with 30 g. of bromine, nearly double the amount required to make tetrabromonaphthazarin. The mixture was allowed to stand for five weeks at room temperature. At the end of this period a yellow product had settled out. Under the microscope the crystals were found to be yellow platelets, highly refractive and mixed with some red needles. The latter were probably naphthazarin since, on heating the product, red fumes began to appear at 180°. Purification was accomplished by recrystallizing from boiling glacial acetic acid, ethyl acetate or toluene. The quinone is difficultly soluble in glacial acetic acid, acetone, chloroform and benzene; nearly insoluble in alcohol. When recrystallized from acetic acid or ethyl acetate, the color changes from yellow to red and the crystalline form from platelets to microscopic needles. The pure substance sublimates at 275–280°. It is insoluble in sodium carbonate solution. Its preparation can be carried out in hot solution.

Anal. Subs., 0.2538: AgBr, 0.3760. Calcd. for $C_{10}O_4Br_4$: Br, 63.46. Found: 63.04.

The diquinone can be reduced and acetylated in one operation using zinc dust and acetic anhydride, yielding diacetyltetrabromonaphthazarin (III).

Dianilide (VI).—This product was prepared in the same manner as (IV), glacial acetic acid, however, being used as solvent. One g. of the diquinone gave 0.7 g. of product. On recrystallizing from glacial acetic acid, it formed brown needles with a metallic luster, subliming at 220–225°. It is easily soluble in alcohol, benzene and glacial acetic acid, less soluble in ether, nearly insoluble in petroleum ether and insoluble in sodium carbonate solution.

Anal. Subs., 0.3062: AgBr, 0.2288. Calcd. for $C_{22}H_{14}O_4Br_2$: 31.97. Found: 31.78.

2,3-Naphthazarin Dichloride (X).—This compound was obtained by Zincke and Schmidt⁷ by chlorinating naphthazarin. We obtained it from tetrahydroxynaphthalene. Two and one-half g. of the latter compound was dissolved in 30 cc. of chloroform and cooled with ice. Dry chlorine was passed in slowly for ten hours. The solution at the end of this time was red, due to a small amount of impurity. The solution was concentrated by blowing off some of the solvent with air. The product was filtered and a small quantity of red crystals was dissolved out on the filter by dropping cold acetone upon the material while the suction was on. The product became pure yellow and melted at 220°.

2,3-Dibromonaphthazarin (VII).—This compound was first made by one of us and Edwards⁸ from tetrahydroxynaphthalene. This preparation was made from naphthazarin. One g. (1 mole) of naphthazarin was dissolved in 25 cc. of glacial acetic acid and treated with 1.5 g. of bromine (slightly less than 2 moles). The solution was boiled for four hours. The product, recrystallized from glacial acetic acid, consisted of red leaves of a metallic luster, melting at 258°; weight, 1.3 g. This product will sublime. The reaction may also be carried out at 70°. No anilido derivative could be obtained. An attempt was made to prepare a Eurhodol. A mixture of 1.75 g. of dibromonaphthazarin and 0.60 g. of *o*-phenylenediamine was dissolved in 200 cc. of absolute alcohol and refluxed for eight hours; 1.5 g. of a purplish-blue compound was obtained. It was nearly insoluble in the usual organic solvents. As it dissolved slightly in glacial acetic acid, large amounts of this were used in an attempt to purify the product. It decomposes at about 225°. The substance was not pure, as the content of bromine was 3% low.

Other Reactions

Action of Phosphorus Trichloride.—Two g. of naphthazarin was mixed with 5 g. of dry sodium carbonate and 75 cc. of phosphorus trichloride and refluxed for thirteen hours. The solution became yellow and some yellow substance collected in the condenser. It was poured into sodium carbonate solution. The dirty red precipitate was insoluble in the usual organic solvents. Its sodium hydroxide solution was intensely blue.

Nitration.—Three methods of nitration were tried: (1) a mixture of boric, sulfuric and nitric acids; (2) sulfuric and nitric acids; (3) acetic and nitric acids. The reactions were carried out at 5°. In each case the product was reduced with stannous chloride and diquinol, melting at 154°, obtained.

Coupling with Amines.—*p*-Chloro-aniline was diazotized and coupled

with naphthazarin. The analysis showed a deficiency of 1.4% of chlorine. We were unable to purify the product further.

We hereby wish to thank the Badische Anilin und Soda-Fabrik of Ludwigshaven on the Rhine for a very generous supply of sublimed naphthazarin.

Summary

1. Recent work shows that the hydroxyl groups in naphthazarin are para to each other and not ortho.

2. The following new derivatives of naphthazarin were prepared: 2,3,6,7-tetrabromonaphthazarin, its diacetate and dianilide; 2,3,6,7-tetrabromodiquinol and its dianilide.

3. The known dichloride of naphthazarin was also made from diquinol and likewise the known dibromonaphthazarin.

4. Certain unsuccessful reactions are noted.

CHAPEL HILL, NORTH CAROLINA

[COMMUNICATION NO. 311 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY]

THE LOWER FATTY ACIDS OF COCONUT OIL

By E. R. TAYLOR AND H. T. CLARKE

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The analysis of coconut oil has been carried out in a variety of ways, each of which has led to a widely different result. A full discussion of the subject is to be found in the paper of Armstrong, Allan and Moore,¹ in which it was clearly shown by these authors that fractionation of the esters of the acids can yield significant results only when the separation of the various components has been so complete as to yield these in substantially pure form, so that the saponification values of the intermediate fractions may legitimately be employed for the estimation of their composition. These authors conducted their fractionation on the ethyl esters obtained from not more than one kilo of coconut oil, and were unable to detect any acid lower than caprylic acid.

We have carried out a systematic fractionation on approximately 130 kilos of methyl esters obtained from commercial coconut oil² by a modification of the method of Haller and Youssoufian.³ The fractionation was carried out repeatedly and systematically until the total amount of fractions intermediate between those of the pure components amounted to

¹ Armstrong, Allan and Moore, *J. Soc. Chem. Ind.*, **44**, 63T (1925).

² This material was stated by its manufacturers (the Procter and Gamble Company) to have been prepared from copra of mixed origin but to be of representative quality.

³ Haller and Youssoufian, *Compt. rend.*, **143**, 803 (1906).

less than 5% of the entire amount. No attempt was made to separate the esters of acids higher than myristic.

Distributing the components of the intermediate fractions pro rata according to the weights and boiling ranges of these, the results indicate the following composition: methyl caproate, 0.48%; methyl caprylate, 8.9%; methyl caprate, 5.7%; methyl laurate, 45.2%; methyl myristate, 16.5%; higher esters, 23.4%. The value for methyl myristate should be slightly higher than is indicated since its separation from the higher esters was not carried to completion. The above percentages are based on the final total weight, which was about 3% lower than that of the weight of the crude ester. The losses, which may be partially accounted for by the presence of alcohol, have thus been distributed through the series.

The purity of the individual esters was checked by determining the melting points of the acids prepared by hydrolysis of the appropriate fractions; in all cases satisfactory agreement with recorded values was obtained.

Attention is drawn to the presence of methyl caproate. Its identity was established by conversion of the free acid through its chloride into the amide, which possessed the same melting point as the amide prepared from synthetic caproic acid and showed no change of melting point on mixing with an authentic sample. The anilide also possessed the melting point recorded in the literature.

Since only 3 g. of distillate passed over below 151° (corr.), it may confidently be asserted that butyric acid is not present in detectable amounts in coconut oil.

Experimental

In 22-liter flasks were placed 8 kg. of coconut oil, 9600 g. of methyl alcohol and 500 g. of sulfuric acid. The mixture was refluxed for forty-eight hours on the steam-bath, allowed to cool to room temperature and the top layer of esters separated. The mixture of esters was placed in a 15 gal. crock and made just neutral to methyl orange with sodium carbonate solution, when 6 liters of a saturated salt solution was stirred into the mixture and allowed to settle. The bottom layer was siphoned off and discarded.

The crude ester (130 kg. from 136 kg. of coconut oil) was distilled under reduced pressure in 7-8 liter portions from a 12-liter flask fitted with a 24cm. column, dividing the distillate into five fractions. Fractionation of these was systematically carried out until the distribution of the various fractions shown in the table was reached. The final distillations of the lowest fractions were carried out under atmospheric pressure.

Samples of the esters were saponified; the resulting free acids showed the following constants: caproic acid, b. p. 204-206° (corr.); caprylic acid, m. p. 14-15°; capric acid, m. p. 30-31°; lauric acid, m. p. 42-43°; myristic

B. p., °C. (corr.)	Product, g.	B. p. (corr.), °C. 7 mm.	Product, g.
To 151	3	121-124	344
151-153	534 (methyl caproate)	124-126	55,153 (methyl laurate)
153-162	41	126-129	596
162-178	49	129-133	132
178-189	25	133-138	799
189-194	75	138-146	485
195-196	10800 (methyl caprylate)	146-155	213
196-199	171	155-157	18,763 (methyl myristate, m. p. 16-17°)
199-204	76		
204-210	83	157-162	786
210-215	76	162-167	895
215-220	96	167-	29,545
220-226	116		
226-232	164		
232-234	6320 (methyl caprate)		
234-242	170		
242-249	254		
249-260	164		
260-	597		

acid, m. p. 53-54°. A sample of the caproic acid was converted by means of thionyl chloride into the acid chloride and the crude product so obtained was added with stirring to concentrated ammonia held below 0° by the addition of ice. The precipitated amide, after washing with dilute ammonia and drying in air, melted at 93-95° and possessed a distinct odor of caproic acid. On recrystallization from toluene the odor was removed and the melting point rose to 98-99°. A sample of authentic caproic acid (prepared from *n*-butyl bromide by the malonic ester synthesis) yielded an amide which also melted at 98-99°.⁴ A mixture of these two amides showed no change in melting point. Another portion of the chloride was converted into the anilide by adding it to a benzene solution of aniline. The benzene solution was washed with dilute acid and dilute alkali and concentrated, when it deposited crystals of the anilide which melted at 94.5-95.5°.⁵

Summary

Systematic fractionation of about 130 kilos of methyl esters of coconut oil acids has been carried out; the results give definite information as to the quantitative distribution of the various lower acids in the original oil. The following acids have been isolated: caproic acid (0.46%), caprylic acid (8.7%), capric acid (5.6%), lauric acid (45.0%), myristic acid (16.5-18%).

ROCHESTER, NEW YORK

⁴ (a) Kelbe, *Ber.*, 16, 1200 (1883), and (b) Hofmann, *Ber.*, 17, 1411 (1884), give m. p. 100°; (c) Autenrieth, *Ber.*, 34, 183 (1901), quotes 98°; (d) Robertson, *J. Chem. Soc.*, 115, 1220 (1919), quotes 101°.

⁵ Kelbe (ref. 4a) gives m. p. 95°; Robertson (ref. 4d) quotes 92°.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYME NE STUDIES. IX. THE NITRATION OF 2-AMINO-*p*-CYME NE¹

BY ALVIN S. WHEELER AND F. P. BROOKS

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The nitration of 2-amino-*p*-cymene or carvacrylamine has not hitherto been undertaken. A pure acetyl derivative was difficult to obtain if the aminocymene was boiled with glacial acetic acid. A quicker and better method recently noted in this Laboratory is to treat an acetone solution of aminocymene with acetyl chloride. The acetyl derivative was nitrated at 0° in sulfuric acid solution with nitric acid. Hydrolysis of the nitro compound gave an aminonitrocymene which is a liquid. Its hydrochloride turns purple readily in the light. The benzoyl derivative of aminocymene was prepared with the hope of more readily obtaining a pure compound for nitration. A nitro derivative was obtained from the benzoate but its hydrolysis was impossible in open vessels. Its reduction gave benzamido-aminocymene. The acetyl derivative and the hydrochloride of the latter were prepared.

Two dyes were obtained by coupling diazotized aminonitrocymene with 2-naphthol and with Neville-Winther's salt.

Experimental Part

2-Aceto-amido-5-nitro-*p*-cymene, $C_9H_7CH_2C_6H_7NHCOCH_3NO_2$.—Nineteen parts of acetyl cymidine, m. p. 71°, was dissolved in 84 parts of sulfuric acid (1.84), cooled to 0° and treated dropwise with 10 parts of 70% nitric acid. The nitration mixture was poured into ice water. The solid product was filtered and washed with much water. It was then broken up into small pieces, washed with sodium hydroxide and recrystallized from hot alcohol. It is usually difficult to get the product into crystalline form; pale yellow prisms, m. p. 148°, very soluble in chloroform, fairly soluble in alcohol, benzene and acetic acid and insoluble in petroleum ether.

Anal. Subs., 0.1816: N_2 , 19.4 cc. (20°, 745 mm.). Calcd. for $C_{12}H_{16}O_4N_2$: N, 11.87. Found: 12.23.

2-Amino-5-nitro-*p*-cymene, $C_9H_7CH_2C_6H_7NH_2NO_2$.—The aceto-amido compound was hydrolyzed with boiling concd. hydrochloric acid. The free base was thrown out with alkali and extracted with ether. The orange-colored oil left after evaporation of the ether was steam distilled. The distillate was saturated with salt and extracted with ether. The yellow liquid left after evaporation of the ether was distilled at atmospheric pressure, a considerable portion decomposing. The pure nitro-amine distilled above 250° and possessed a sweet taste.

Anal. Subs., 0.2009: N_2 , 25.8 cc. (23°, 752 mm.). Calcd. for $C_{10}H_{14}O_2N_2$: N, 14.43. Found: 14.24.

¹ This paper is an abstract of a thesis submitted to the faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1926.

Hydrochloride.—The hydrochloride crystallizes in clusters of white needles which turn purple in the light. It is quickly hydrolyzed by alcohol or the moisture of the air, turning yellow. It was recrystallized from alcohol containing hydrochloric acid. It was rapidly dried and analyzed by titration, using phenolphthalein as indicator.

Anal. Subs., 0.1000, 0.1000: 21.44, 21.44 cc. *N*/50 NaOH. Calcd. for $C_{10}H_{14}O_2N_2 \cdot HCl$, 15.81. Found: 15.71, 15.71.

2-Benzamido-5-nitro-*p*-cymene, $C_6H_2CH_2C_6H_7NHCOC_6H_5NO_2$.—Aminocymene was benzoylated in the usual way. The melting point of the product remained at 90.5° after repeated recrystallizations from hot alcohol although Andrews² gives 96.5°. The product was nitrated by dissolving 10 g. in 50 cc. of concd. sulfuric acid, cooling to 0° and slowly adding 10 g. of concd. nitric acid, holding the temperature at 0°. The mixture was poured into 600 cc. of water containing ice. The yellow precipitate was filtered, well washed with water and dried on a porous plate; weight, 36 g. A preparation with 30 g. gave a yield of 95 g. These are very high yields but recrystallizing from alcohol brings the yields down at once to expected figures. About 16 g. dissolve in 100 cc. of boiling alcohol and 2 g. remain in solution at room temperature. The crystals are very pale yellow, six-sided prisms which melt at 215–218°.

Anal. Subs., 0.2516: N_2 , 21.2 cc. (23°, 754 mm.). Calcd. for $C_{17}H_{18}O_2N_2$: N , 9.39. Found: 9.39.

2-Benzamido-5-amino-*p*-cymene, $C_6H_2CH_2C_6H_7NHCOC_6H_5NH_2$.—Ten g. of benzamidonitrocymene was reduced in alcoholic solution with tin and hydrochloric acid. The alcohol was evaporated off, the residue taken up with water and the solution made strongly alkaline. The solution was extracted with ether, the latter evaporated off and the yellow residue dissolved in hydrochloric acid and the solution filtered and treated with ammonia. The free base was purified by reprecipitating several times. It is a pale yellow solid, melting at 115°. It is soluble in alcohol and acetic acid, less soluble in ether and insoluble in water. The yellow alkaline solution rapidly becomes bluish. The ether solution is yellow with a bluish fluorescence.

Anal. Subs., 0.2333: N_2 , 23 cc. (29°, 757 mm.). Calcd. for $C_{17}H_{18}ON_2$: N , 10.53. Found: 10.66.

Hydrochloride.—Hydrogen chloride was passed into an ether solution of the amine, giving pale yellow crystals which deepen in color on drying. It melts with decomposition above 200°.

Anal. Subs., 0.1000: 33 cc. of *N*/10 NaOH. Calcd. for $C_{17}H_{20}ON_2HCl$: HCl , 11.97. Found: 12.03.

2-Benzamido-5-aceto-amido-*p*-cymene was prepared by boiling the 5-amino compound with glacial acetic acid for ten hours. The solution was concentrated and the acid neutralized. The precipitate was dissolved in ether, from which it separated as a yellow powder, melting at 120°. Analysis for nitrogen gave 8.11% against a theoretical value of 9.04%, showing the compound to be impure, but scarcity of material prevented further purification.

New Azo Dyes

1-(5-Nitrocarvacrylazo)-2-naphthol, $C_6H_2CH_2C_6H_7NO_2N_2C_{10}H_6OH$.—Diazotized nitro-aminocymene was coupled with 2-naphthol in the usual way. The dye was recrystallized from glacial acetic acid. It formed well-shaped deep red prisms melting at 245°.

Anal. Subs., 0.2145: N_2 , 23.4 cc. (20°, 752 mm.). Calcd. for $C_{20}H_{19}O_2N_2$: N , 12.04. Found: 12.30.

² Andrews, *J. Ind. Eng. Chem.*, 10, 453 (1918).

2-(5-Nitrocarvacrylazo)-1-naphthol-4-sulfonic Acid, $C_{16}H_9CH_3C_2H_4NO_2N_3C_{10}H_7OHSO_3ONa$.—Nitro-aminocymene was diazotized and coupled with Neville-Winther's salt. The product was salted out of solution. It is a red dye, soluble in water and alcohol and was recrystallized from alcohol.

Anal. Subs., 0.1511: N_3 , 13 cc. (24°, 753 mm.). Calcd. for $C_{26}H_{19}O_4N_3SNa$: N, 9.33. Found: 9.51.

The Constitution of Aminonitrocymene

It is possible for the nitro group to enter any of the vacant positions, 3, 5 and 6. Position 6 is eliminated because the nitro compound does not correspond to the 2-amino-6-nitro-*p*-cymene described by one of us and Harris.³ Its acetyl derivative melts at 115° and not 148°. Similarly the benzoyl derivatives are wide apart in melting points. The expectation is that the nitro group will enter para to the amino group, that is, Position 5. That this is the case is indicated by our conversion of the acetyl derivative into 2,5-diaceto-amido-*p*-cymene, described by Kehrmann and Messinger,⁴ who obtained it from thymoquinonedioxime. We reduced aceto-amidonitrocymene with tin and hydrochloric acid and purified the hydrochloride of 2-aceto-amido-5-amino-*p*-cymene.

Anal. Subs., 0.1000: 44.9 cc. *N*/10 NaOH. Calcd. for $C_{17}H_{18}ON_2HCl$: HCl, 16.09. Found: 16.35.

It is white but readily turns pink. The free base quickly turns to a blue compound. The diacetyl derivative was obtained by boiling with acetic anhydride and sodium acetate. The product, recrystallized from alcohol, melted at 260°, which is the melting point given by Kehrmann and Messinger for 2,5-diacetylamido-*p*-cymene.

Summary

1. 2-Amino-5-nitro-*p*-cymene was obtained by the nitration of 2-aceto-amido-*p*-cymene.
2. Its constitution was determined by its conversion into 2,5-diaceto-amido-*p*-cymene, previously made from thymoquinonedioxime.
3. The following new compounds were made: 2-aceto-amido-5-nitro-*p*-cymene and its hydrochloride; 2-benzamido-5-nitro-*p*-cymene; 2-benz-amido-5-amino-*p*-cymene, its hydrochloride and acetate; the hydrochloride of 2-aceto-amido-5-amino-*p*-cymene.
4. Two azo dyes were made by coupling the aminonitrocymene with 2-naphthol and with 1-naphthol-4-sulfonic acid.

CHAPEL HILL, NORTH CAROLINA

³ Wheeler and Harris, *THIS JOURNAL*, 49, 496 (1927).

⁴ Kehrmann and Messinger, *Ber.*, 23, 3557 (1890).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PIPERIDINE DERIVATIVES

IV. SUBSTITUTED PIPERIDINE-ALKYL BENZOATES AND PARA-AMINOBENZOATES

By S. M. McELVAIN

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The numerous investigations of the amino-alkyl benzoate type of local anesthetics have produced a few compounds in which the piperidine nucleus comprises the amino group. Pyman¹ prepared piperidyl² ethylbenzoate. It was found to have local anesthetic properties but a rather high toxicity. Brill³ prepared N-piperidinopropylbenzoate and mentioned that it had local anesthetic properties. Recently the piperidino-ethyl esters of propylaminobenzoic acid and methoxy-ethylaminobenzoic acid have been described⁴ as local anesthetics. Since the completion of the work described below, Barnes and Adams⁵ have described the *p*-aminobenzoates of N-(β -hydroxy-ethyl)-piperidine, N-(γ -hydroxypropyl)-piperidine, β -(β -carbomethoxypiperidyl)-ethyl alcohol and γ -(β -carbomethoxypiperidyl)-propyl alcohol. They were local anesthetics, the substituted piperidine derivatives being less effective than the unsubstituted.

It seemed probable that the presence of certain substituent groups in the piperidine nucleus of such compounds would produce a definite effect on their physiological properties. Accordingly, a number of substituted piperidino-alkylbenzoates were prepared and submitted for pharmacological study. These compounds do not form a well-defined series, but are merely some of the possible types that offered a particular preparational advantage on account of the availability of the necessary substituted piperidines. Work is at present under way which will, it is hoped, sufficiently complete the various indicated series to point to some fairly definite conclusions relative to the effect of structure on physiological action.

This paper deals with the preparation and the preliminary pharmacological study of the following compounds: γ -piperidinopropylbenzoate (I), γ -2-methylpiperidinopropylbenzoate (II), γ -2-propylpiperidinopropylbenzoate (III), γ -3-methylpiperidinopropylbenzoate (IV), β -3-methylpiperidino-ethylbenzoate (V), γ -3-carbethoxypiperidinopropylbenzoate (VI),

¹ Pyman, *J. Chem. Soc.*, 93, 1793 (1908).

² The nomenclature used in this paper is that suggested by Meyer and Jacobson and designates as "piperidino" the radical formed by dropping the hydrogen from the nitrogen atom of piperidine and as "piperidyl" the radical formed by dropping a hydrogen from one of the carbon atoms of piperidine. By this nomenclature Pyman's compound would be "piperidino-ethyl benzoate."

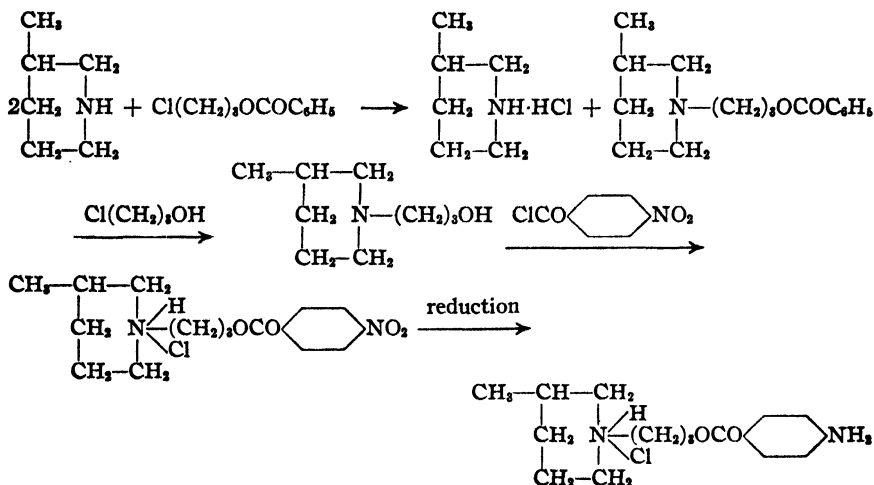
³ Brill, *THIS JOURNAL*, 47, 1134 (1925).

⁴ Brit. pat. 241,767; *C. A.*, 20, 3539 (1926).

⁵ Barnes with Adams, *THIS JOURNAL*, 49, 1307 (1927).

γ -piperidinopropyl-*p*-aminobenzoate (VII), γ -3-methylpiperidinopropyl-*p*-aminobenzoate (VIII), γ -3-carbethoxypiperidinopropyl-*p*-aminobenzoate (IX). The unsubstituted piperidino derivatives (I and VII) were included in the above list for comparison. All of these substances were isolated and used as the hydrochlorides.

The benzoates were most conveniently prepared by the condensation of the substituted piperidine with a chloro-alkylbenzoate. The *p*-aminobenzoates were prepared by first condensing the piperidine with trimethylene chlorohydrin, acylating the resulting piperidinopropyl alcohol with *p*-nitrobenzoyl chloride, and finally reducing the resulting *p*-nitrobenzoate catalytically to the *p*-aminobenzoate. These reactions are represented with 3-methylpiperidine, thus



A marked difference in the reactivity of the 2 substituted piperidines and the 3 substituted piperidines was noted in the above condensation. The 3-methyl- and 3-carbethoxypiperidines reacted practically completely with γ -chloropropylbenzoate when heated for twenty to thirty minutes at 100°. The amount of reaction was determined by the quantity of the hydrochloride of the secondary amine that was obtained when the reaction mixture was diluted with ether. Under the same conditions there was hardly any reaction between the 2-methyl- or 2-propylpiperidine and the chloro ester. It was found necessary to heat these reactants for one to three hours at temperatures of 125–150° in order to produce a satisfactory reaction.

Experimental

3-Carbethoxypiperidine (ethyl nipecotate).—This compound was prepared by the procedure described by McElvain and Adams.⁶

⁶ McElvain and Adams, *THIS JOURNAL*, **45**, 2745 (1923).

3-Methylpiperidine.—3-Methylpyridine (β -picoline) was prepared from glycerol ammonium phosphate and phosphorus pentoxide according to the method of Schwarz.⁷ The hydrochloride was prepared and reduced catalytically, using the same procedure as that employed for the preparation of 3-carbethoxypiperidine. The 3-methylpiperidine so obtained boiled at 123–126°.

2-Methylpiperidine.—2-Methylpyridine (α -picoline) was isolated from the picoline fraction of coal tar bases which boiled at 127–132° by the method of Heap, Jones and Speakman.⁸ It was reduced in a manner similar to that used for 3-methylpyridine. The 2-methylpiperidine boiled at 114–116°.

2-Propylpiperidine.—This base was obtained by the action of aqueous sodium hydroxide on a sample of Merck's coniine hydrobromide. After drying it boiled at 164–166°.

Substituted Piperidino-alkylbenzoate Hydrochlorides.—The general procedure for the preparation of these compounds consisted of heating together 2 molecular equivalents of the secondary amine (a substituted piperidine) and 1 molecular equivalent of the chloro-alkyl benzoate. The reaction mixture was cooled, diluted with several volumes of ether and the precipitated secondary amine hydrochloride filtered off. From the ether solution the tertiary amine was precipitated with dry hydrogen chloride as the hydrochloride, which was further purified by recrystallization from an alcohol-ether mixture.

There was a marked difference between the condensations of the 2 substituted piperidines and those of the other piperidines which were used with the chloro ester. It was found that the unsubstituted piperidine and 3 substituted piperidines condensed quite completely with the chloro ester in twenty to thirty minutes at 100°, while the 2 substituted piperidines required temperatures of 125–150° for two to three hours. Even under these conditions the condensations of the 2 substituted piperidines were sufficiently incomplete to cause considerable secondary amine hydrochloride to be mixed with the tertiary amine hydrochloride. In such cases it was necessary to treat the mixed hydrochlorides with dilute aqueous sodium hydroxide and shake the resulting aqueous suspension of the free bases with benzoyl chloride. The tertiary amine was then extracted from this

TABLE I
SUBSTITUTED PIPERIDINO-ALKYLBENZOATE HYDROCHLORIDES

Piperidino-alkyl group	M. p., °C.	Analyses, Cl, %	
		Calcd	Found
γ -Piperidinopropyl	186–188 ^a	12.52	12.58
γ -2-Methylpiperidinopropyl	167–169	11.93	11.96
γ -2-Propylpiperidinopropyl	184–186	10.90	10.84
γ -3-Methylpiperidinopropyl	178–180	11.93	11.90
β -3-Methylpiperidino-ethyl	134–136	12.52	12.72
γ -3-Carbethoxypiperidinopropyl	161–163	10.01	10.10

^a Brill (ref. 3) describes this compound as melting at 192°.

⁷ Schwarz, *Ber.*, 24, 1676 (1891).

⁸ Heap, Jones and Speakman, *This Journal*, 43, 1936 (1921).

reaction mixture with ether and reprecipitated as the hydrochloride. This treatment, followed by recrystallizations from an alcohol-ether mixture, gave quite pure products. The yields of the recrystallized products in the case of the 2 substituted piperidino compounds were 35-40%, while in the case of the piperidino and 3 substituted piperidino compounds they amounted to 60-65%.

γ -Substituted Piperidinopropyl-*p*-nitrobenzoate Hydrochlorides.—Two molecular equivalents of the piperidine and 1 molecular equivalent of trimethylene chlorohydrin were heated together at 100° for thirty minutes. The reaction mixture was cooled, treated with several volumes of ether and the precipitated secondary amine hydrochloride filtered off. The piperidinopropyl alcohol was precipitated from the ether solution as the hydrochloride, the ether decanted off and the precipitate, a sirupy, amorphous mass, dried under diminished pressure at 150° for twenty minutes. To this dried hydrochloride 1.5 molecular equivalent of *p*-nitrobenzoyl chloride was added and the mixture heated until the evolution of hydrogen chloride had ceased. The reaction mixture was cooled, diluted with ether and the precipitate allowed to crystallize. Recrystallizations from an alcohol-ether mixture gave pure products. The yields were 50-63%.

TABLE II

 γ -SUBSTITUTED PIPERIDINOPROPYL-*p*-NITROBENZOATE HYDROCHLORIDES

Piperidinopropyl group	M. p., °C.	Analyses, Cl, %	
		Calcd.	Found
γ -Piperidinopropyl	201-203	10.80	10.68
γ -3-Methylpiperidinopropyl	190-192	10.36	10.46
γ -3-Carbethoxypiperidinopropyl	177-179	8.86	9.03

γ -Substituted Piperidinopropyl-*p*-aminobenzoate Hydrochlorides.—A solution of 15 g. of the piperidinopropyl-*p*-nitrobenzoate hydrochloride in 150 cc. of absolute alcohol was reduced catalytically with 0.2 g. of catalyst by the method which has been described for the 1-alkyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoates.⁹ After reduction the solvent was evaporated off and the remaining monohydrochloride of the *p*-aminobenzoate recrystallized from an alcohol-ether mixture. The yields were 65-75%.

TABLE III

 γ -SUBSTITUTED PIPERIDINOPROPYL-*p*-AMINOBENZOATE HYDROCHLORIDES

Piperidinopropyl group	M. p., °C.	Analyses, Cl, %	
		Calcd.	Found
γ -Piperidinopropyl	214-216	11.90	12.05
γ -3-Methylpiperidinopropyl	158-160	11.03	10.90
γ -3-Carbethoxypiperidinopropyl	113-115	9.64	9.90

Pharmacological Report

These anesthetics are being studied pharmacologically by Mr. Charles L. Rose of the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. A brief report of a portion of this work is included in this paper.

The anesthetic efficiencies were determined in the usual way by the application of a 2% solution of the anesthetic to the rabbit's cornea and

⁹ McElvain, *THIS JOURNAL*, **48**, 2240 (1926).

noting the duration of anesthesia. The toxicities were determined by subcutaneous injection into white mice and also by intravenous injection into white rats. The toxicity values for the maximum tolerated dose and the minimum lethal dose are expressed in milligrams per kilogram body weight of the animals. The results of these pharmacological studies are summarized in Table IV and the various anesthetics are designated by the Roman numerals which accompany them in the introductory portion of the paper. The corresponding values for cocaine and procaine are included for comparison.

TABLE IV
PHARMACOLOGICAL DATA

Compound	Average duration of anesthesia, min.	Subcutaneous toxicity to white mice (mg./kg.)			Intravenous toxicity to white rats (mg./kg.)		
		M. T. D.	M. L. D.	No. of mice used	M. T. D.	M. L. D.	No. of rats used
I	0	400	450	8	15	17.5	10
II	15	800	900	21	15	17.5	9
III	8	600	700	20	7.5	10	10
IV	11	450	500	7	20	25	9
V	0	3000	3500	29	25	30	11
VI	0	750	800	18	30	35	8
VII	0	50	100	10	7.5	10	11
VIII	10	200	250	13	25	30	17
IX	0	1200	1300	19	30	35	10
Cocaine	29	200	250	18	15	17.5	12
Procaine	0	900	1000	17	45	50	10

Discussion of the Pharmacological Data

It is interesting to note that the only compounds in the above group that show any mucous membrane anesthesia are those in which an alkyl group is substituted in the piperidine nucleus. Those compounds (VI and IX), containing a carbethoxy substituent in the piperidine nucleus show no anesthetic action towards mucous membranes. These findings correspond to those of Barnes and Adams⁵ for the analogous 3-carbomethoxypiperidino derivative. The difference between the anesthetic action of Compounds IV and V is striking. Compound IV, which is γ -3-methylpiperidino-propylbenzoate, possesses distinct local anesthetic action, while the β -3-methylpiperidino-ethylbenzoate (V) shows no such action. Apparently this loss of anesthetic effect is caused in V by decreasing the number of methylene groups between the nitrogen and the benzoyl group from three to two.

Very few generalizations can be made from the toxicity data for this group of compounds. It is apparent that the substituted piperidino derivatives are less toxic than the corresponding unsubstituted piperidino derivatives. With the exception of IX, the *p*-aminobenzoates are more toxic subcutaneously than the corresponding benzoates. The same difference

was observed between the 1-alkyl-3-carbethoxy-4-piperidylbenzoates and *p*-aminobenzoates.¹⁰ In the above data there does not seem to be much correlation between the subcutaneous and absolute (intravenous) toxicities.

Summary

1. Several substituted piperidino-alkylbenzoates and *p*-aminobenzoates have been prepared and described.

2. The alkyl substituted piperidino compounds which contain three methylene groups between the piperidine nitrogen and the benzoyl group possess local anesthetic action, while the corresponding unsubstituted and carbethoxy substituted piperidino derivatives show no local anesthetic activity.

3. In general, the substituted piperidino derivatives are less toxic than the corresponding unsubstituted piperidino derivatives.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE COLOUR CHEMISTRY DEPARTMENT, TECHNICAL COLLEGE, HUDDERSFIELD, ENGLAND]

THE MERCURATION OF *o*-NITROPHENOL

BY HERBERT HENRY HODGSON

RECEIVED JULY 2, 1927

PUBLISHED NOVEMBER 5, 1927

Iodination of *o*-nitrophenol by the aid of yellow mercuric oxide was found by the author¹ to take place preferentially in the 4 as compared with the 6 position whether the medium employed was alcohol or glacial acetic acid, and in addition considerable di-iodination took place even when a deficiency of iodine was used. In consequence it became of interest to ascertain whether mercuration would exhibit a like preference.

Previous work on this subject by Hantzsch and Auld² established that when an alcoholic solution of *o*-nitrophenolate (1 mole) and aqueous mercuric acetate (1 mole) were boiled together, the mono-mercuri product formed yielded *p*-bromo-*o*-nitrophenol when brominated, thereby establishing mercuration in the 4 position. Later Raiziss and Proskouriakoff³ proved that considerable dimercuration occurred under the above conditions and, although the various products were not orientated by them, tacit assumption of mercuration in the 4 position was made for the mono-mercuri products.

In the present investigation mercuration has been effected both by fusion of *o*-nitrophenol with mercuric acetate and also according to the directions of Raiziss and Proskouriakoff. In the former case marked

¹⁰ McElvain, *THIS JOURNAL*, **48**, 2184, 2241 (1926).

¹ Hodgson, *J. Chem. Soc.*, 1927, 1141.

² Hantzsch and Auld, *Ber.*, **39**, 1105 (1906).

³ Raiziss and Proskouriakoff, *THIS JOURNAL*, **44**, 787 (1922).

preference was shown for mercuration in the 6 position and practically no dimercuration occurred, whereas in aqueous alcoholic solution substitution in the 4 position accompanied by considerable dimercuration took place.

Orientations were established by conversion of the mercured products into the corresponding iodonitrophenols.

The 6- and 4-acetoxymercuri-2-nitrophenols were readily converted into the 6- and 4-fluoro-, chloro-, bromo- and iodomercuri-2-nitrophenols, all of which were lighter in color than *o*-nitrophenol itself, the depths of shade increasing gradually from fluoro (almost colorless) to chloro (very pale brownish-yellow), bromo (pale yellow) and iodo (almost as deep a yellow as *o*-nitrophenol). Further, the 6-acetoxy- and 6-halogenomercuri-2-nitrophenols appear to be somewhat paler than the 4 substituted isomerides and, moreover, possess lower melting points and lesser solubilities in alcohol and acetic acid.

Experimental

6-Acetoxymercuri-2-nitrophenol.—An intimate mixture of *o*-nitrophenol (15 g.) and mercuric acetate (3 g.) was heated gradually to 150° during one hour, and kept at 140–150° for four hours with frequent shaking. The reaction product was mixed with a saturated solution of sodium chloride and steam distilled, when unchanged *o*-nitrophenol was recovered (12 g.) and a non-volatile residue (2 g.) obtained from which 6-chloromercuri-2-nitrophenol was removed by repeated extraction with boiling alcohol. The light brown almost colorless residue was dissolved as completely as possible in dilute sodium hydroxide, the solution filtered, reprecipitated by acetic acid and the product crystallized from glacial acetic acid, in which it is only moderately soluble, giving pale brownish-yellow, almost colorless micro clusters which do not appear to melt below 300°.

Anal. Calcd. for $C_6H_5O_2NHg$: N, 3.5. Found: 3.6.

When an aqueous suspension of 6-acetoxymercuri-2-nitrophenol is gently warmed for about 30 minutes with excess iodine dissolved in aqueous potassium iodide, almost the whole is converted into 6-iodo-2-nitrophenol (1 g. gives 0.62 g.; calcd. 0.71 g.), which is removed by steam distillation and crystallized from dilute alcohol, giving characteristic plates, m. p. 110°.

Anal. Calcd.: I, 47.9. Found: 47.7.

This product, when treated in glacial acetic acid solution with iodine and yellow mercuric oxide, was converted quantitatively into 4,6-di-iodo-2-nitrophenol. When the steam-volatile product was collected in small fractions, the first one had a melting point of 102° and appeared to contain a certain amount of 4-iodo-2-nitrophenol, recognized by microscopic examination. A negligible amount of 4,6-di-iodo-2-nitrophenol was detected in the iodination experiment above, which indicated that almost no dimercuration had taken place.

4-Acetoxymercuri-2-nitrophenol, prepared according to the directions of Raiziss and Proskouriakoff,³ was treated with iodine as above and afforded a mixture of 4,6-di-iodo- and 4-iodo-2-nitrophenols, with a little 6-iodo-2-nitrophenol. The former, which was present in considerable amount, thus confirms Raiziss and Proskouriakoff's observation³ with respect to the fairly extensive dimercuration which takes place under these conditions. The two latter products were separated by steam distillation, fractionally crystallized from alcohol and identified by microscopic examination, confirma-

tion forthcoming by iodination of all the fractions to 4,6-di-iodo-2-nitrophenol, exclusively.

6- and 4-Halogenomercuri-2-nitrophenols.—These products were precipitated by the addition of the requisite halogen acid to solutions of the sodium 6- and 4-hydroxymercuri-2-nitrophenols prepared according to the directions of Raiziss and Proskouria-koff³ except in the cases of the 6- and 4-iodomercuri-2-nitrophenols, which were precipitated by the addition of dilute sulfuric acid to solutions of the above sodium salts in which a large excess of potassium iodide had been dissolved. The 4-halogeno-mercuri compounds were all slightly deeper in color and more soluble in alcohol and acetic acid than the 6 isomerides and all possessed higher melting points where these existed.

For convenience and to abbreviate description the crystalline form, color and melting points of the 6 and 4 compounds are given in Table I below. Both sets were crystallized from alcohol.

Sodium-6-hydroxymercuri-2-nitrophenolate gives scarlet-red crystals, while the crystals of the 4 compound are a deeper red.

Anal. Calcd. for $C_6H_4O_4NNaHg$: N, 3.7. Found: 3.8.

TABLE I
HALOGENO-MERCURI-2-NITROPHENOLS

Name	M. p., °C.	—6 Isomer—		M. p., °C.	—4 Isomer—		Composition, % Calcd. Found	
		Color	Crystal form		Color	Crystal form		
Fluoro	187	Pale yellow	Plates	195	...	Micro plates	N = 3.9	4.0
Chloro	185*	Pale yellow- ish-brown	Rect. plates	205	Creamy yellow	Micro clusters	Cl = 9.5	9.5
Bromo	177	Pale yellow	Plates	236	...	Needles	Br = 19.1	18.9
Iodo	215	Deep yellow	Needles	>300	Bright yellow	Micro needles	I = 27.3	27.0

* Crude product, m. p. 175°; contained some of the 4 isomer as shown by its reaction with iodine, etc. The pure product, m. p. 185°, gave only the 6 isomer.

Summary

Fusion of *o*-nitrophenol with mercuric acetate gives mainly 6-acetoxymercuri-2-nitrophenol. When solvent media are employed, 4-acetoxy-2-nitrophenol is formed preferentially, accompanied, however, by appreciable amounts of 4,6-diacetoxymercuri-2-nitrophenol.

HUDDERSFIELD, ENGLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE FORMATION OF TRIPHENYLMETHYL PEROXIDE FROM CARBON DIOXIDE AND PHENYLMAGNESIUM BROMIDE

BY F. F. BLICKE

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Several years after the discovery by Grignard¹ that carboxylic acids can be prepared from carbon dioxide and alkyl magnesium halides Meyer and Tögel² undertook a detailed study of the action of carbon dioxide on phenyl magnesium bromide. They obtained benzoic acid and triphenylcarbinol as principal products and, in addition, varying amounts of benzene, biphenyl, triphenylmethane and phenol. Furthermore, a small amount of a colorless, crystalline, ether-insoluble material was found. This substance melted at 186° and remained unidentified. Meyer and Tögel also stated that their reaction mixtures were colored. Schroeter³ was able to show that benzophenone is another product formed in this synthesis and he too obtained the ether-insoluble product. From the data which were given we suspected that the unidentified compound might have been triphenylmethyl peroxide, formed by oxidation of triphenylmethyl present in the reaction mixture.

We allowed carbon dioxide to react with phenylmagnesium bromide according to the directions of the above-mentioned investigators and proved conclusively that triphenylmethyl peroxide was present among the reaction products.

A number of unsuccessful experiments were performed in the attempt to discover the reaction by which triphenylmethyl was formed. For example, $C_6H_5COOMgBr$ and $(C_6H_5)_3COMgBr$ were heated, respectively, with phenylmagnesium bromide in ether and the effects of small amounts of magnesium and iodine⁴ upon the reaction mixtures were tested. Although we were unable to determine just how the free radical was formed, it seems probable that triphenylmethyl was produced in some way from triphenylcarbinol, or rather from its $MgBr$ derivative.⁵

By the interaction of carbon dioxide and a cold ether solution of α -naphthylmagnesium bromide, α -naphthoic acid was obtained in good yield. By the use of a hot solution of the Grignard reagent, we hoped that the reaction would proceed further with the formation of the tertiary carbinol

¹ Grignard, *Ann. chim. phys.*, (7) 24, 255 (1901).

² Meyer and Tögel, *Ann.*, 347, 55 (1906).

³ Schroeter, *Ber.*, 36, 3006 (1903).

⁴ (a) Gomberg and Bachmann, *THIS JOURNAL*, 49, 236 (1927); (b) Boyd and Hatt, *J. Chem. Soc.*, 131, 904 (1927).

⁵ Stadnikoff, *Ber.*, 57, 5 (1924), obtained triphenylmethyl peroxide from the interaction of the $MgBr$ derivative of triphenylcarbinol and ethyl formate. The exact mechanism of this reaction has not been established.

and possibly the free radical. A compound claimed to be tri- α -naphthylcarbinol has been described by Schmidlin and co-workers⁶ and also by Tschitschibabin;⁷ the former investigator allowed naphthoyl chloride to react with more than two equivalents of naphthylmagnesium bromide, the latter added naphthylmagnesium bromide to dinaphthyl ketone. However, judging from the remarkable properties ascribed to this compound, it seems to us that these investigators could not have had the pure carbinol. Schmidlin and Massini state that the compound contains a very unreactive hydroxyl group and that the usual reagents which convert tertiary carbinols into their respective chlorides are without action. Tschitschibabin maintains that at ordinary temperature the carbinol spontaneously absorbs oxygen and is oxidized by potassium permanganate to α -naphthyl-di- α , α -naphthofluoryl alcohol. When treated with iodine the carbinol iodide is said to have been formed. As Schmidlin⁸ himself points out it is strange that it was found impossible to convert the carbinol iodide, or bromide, into either the original carbinol or into the free radical. Judging from the properties of diphenyl- α -naphthylcarbinol⁹ and phenyl-di- α -naphthylcarbinol,¹⁰ it might be predicted that tri- α -naphthylcarbinol would possess a very reactive hydroxyl, so reactive, in fact, that the carbinol as well as its derivatives such as $(C_{10}H_7)_3COMgBr$, a compound which would result from the Grignard synthesis, would tend to undergo very readily various types of changes, especially fluorenation. The absorption of oxygen and iodine and the decolorization of potassium permanganate at ordinary temperature are reactions which are foreign to any simple tertiary aromatic carbinols hitherto described. Finally, tri- α -naphthylcarbinol might be expected to yield an intense blue or violet solution when treated with concentrated sulfuric acid; Schmidlin and Tschitschibabin state that their compounds are colored orange-red or yellow by this reagent.

From the interaction of carbon dioxide and a hot ether solution of α -naphthylmagnesium bromide we obtained naphthoic acid and a red oil from which no crystalline products could be obtained.

We then attempted to prepare the carbinol from naphthylmagnesium bromide and di- α -naphthyl ketone. After decomposition of the reaction mixture with ice and ammonium chloride, a colorless material quickly deposited from the ether layer. This substance decolorized solutions of iodine and of potassium permanganate at ordinary temperature and dissolved in sulfuric acid with the formation of a red solution. These ob-

⁶ (a) Schmidlin and Massini, *Ber.*, **42**, 2397 (1909); (b) Schmidlin and Bergman, *ibid.*, **45**, 3203 (1912).

⁷ Tschitschibabin, *J. prakt. Chem.*, **84**, 769 (1911).

⁸ Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1913, p. 163.

⁹ (a) Gomberg, *Ber.*, **37**, 1637 (1904); (b) Acree, *Ber.*, **37**, 624 (1904).

¹⁰ Schoepfle, *THIS JOURNAL*, **44**, 188 (1922).

servations correspond to those of Tschitschibabin but in our opinion the material is not tri- α -naphthylcarbinol, or it contains only very little of this substance.

Since further work on this compound seems impossible at present we are obliged to present our results in an unfinished state.

Experimental Part

The Formation of Triphenylmethyl Peroxide.—Phenylmagnesium bromide was prepared from 6.2 g. of magnesium turnings, 40 g. of bromobenzene, 120 cc. of ether and a crystal of iodine. A rapid stream of dry carbon dioxide was then passed through the solution. At first no noticeable change took place; later the mixture became somewhat warm and colorless crystals were deposited upon the walls of the flask. After one and one-half hours a considerable amount of gummy precipitate had formed. The mixture was then decomposed with ice and slightly more than the calculated amount of dilute hydrochloric acid. After decomposition had been effected a deep orange ether layer was obtained. A small amount of crystalline substance floated between the ether and water layers. When the clear ether solution was separated and shaken with air it became noticeably lighter in color and a colorless, crystalline material precipitated. This was washed with ether and recrystallized twice from xylene; m. p. 184°. A portion of this substance was mixed with triphenylmethyl peroxide obtained from triphenylchloromethane, silver and air; the mixture melted at 185–186°. The largest yields of peroxide were obtained when the solution of phenylmagnesium bromide was heated during the addition of carbon dioxide; the reaction mixture then turned a permanganate color during the course of the reaction. The crude peroxide, varying in weight from 1 to 2 g., contained a considerable amount of magnesium salts which could only be removed by several recrystallizations. When the solution of the Grignard reagent was cooled with ice, the mixture remained colorless during the reaction with carbon dioxide, and upon the addition of water and dilute mineral acid, benzoic acid and some triphenylcarbinol were obtained as the principal reaction products but no peroxide seems to have been formed.

α -Bromonaphthalene.—The bromonaphthalene used in our experiments was carefully purified material. At first a technical grade of this substance was purchased and subjected to several fractional distillations. However, the separation of the monobromonaphthalene from naphthalene, dibromonaphthalene and bromine and hydrogen bromide addition products which were present in the technical product required considerable time. We finally prepared the bromonaphthalene by the following method which differs in several essential respects from the methods commonly used.¹¹ Carbon tetrachloride was substituted for the poisonous and inflammable carbon disulfide; $\frac{3}{4}$ of a molecular equivalent of bromine was used instead of one whole equivalent; the crude bromonaphthalene was fractionated under ordinary pressure instead of under diminished pressure. The use of carbon tetrachloride as a solvent enabled us to brominate in a one-phase system, hence mechanical stirring was unnecessary. By the use of the above amount of bromine the yield of monobromonaphthalene, based on bromine, was as large as that obtained in other processes in which

¹¹ "Organic Syntheses," John Wiley and Sons, Inc., 1921, Vol. I, p. 36.

one whole equivalent of bromine is used; moreover, dibromonaphthalene, a product which represents a loss of both bromine and naphthalene, was formed only in negligible amount. The bromine and hydrogen bromide addition products formed during bromination are surprisingly difficult to decompose; the desired decomposition of these products is always effected by distillation under ordinary pressure but they often remain undecomposed, to some extent at least, during distillation under diminished pressure.

One thousand g. of technical naphthalene and 1500 cc. of carbon tetrachloride were put into a 5-liter flask, the stopper of which was fitted with a reflux condenser and a dropping funnel. The hydrogen bromide evolved during the reaction was led through the condenser into water. One hundred and fifty cc. of bromine was added in 25cc. portions during the course of two hours and the flask was shaken occasionally. A slow, regular evolution of hydrogen bromide began and all of the naphthalene soon dissolved. The remainder of the bromine, 150 cc., was added in 25cc. portions during the course of twenty-four hours. After all of the bromine had been added the mixture was allowed to stand for one day. Two hundred g. of technical sodium hydroxide dissolved in 400 cc. of hot water was then added and the alkaline mixture subjected to steam distillation. After the solvent had been removed, the oily residue was separated and dried with solid sodium hydroxide. The crude product was fractionated under ordinary pressure into four portions and, since hydrogen bromide and bromine were evolved, each fraction was treated with hot concentrated sodium hydroxide solution and then refractionated several times. Most of the unchanged naphthalene was removed from the lowest-boiling portion by filtration. The fourth fractionation of the portion which had boiled at 270–275° under 740 mm. yielded 730 g. of monobromonaphthalene which was collected at 271–274°. From other experiments the yields of bromonaphthalene were 755 g. and 760 g., respectively. Small fractions of low- and high-boiling material obtained from three experiments were united and refractionated. One hundred and fifty g. of pure bromonaphthalene was obtained. The yields given above, therefore, are increased by approximately 50 g., respectively, and correspond to 63, 65 and 65%, respectively, of the calculated amounts based on bromine.

α -Naphthoic Acid.—Acree¹² claims to have obtained an almost theoretical yield of α -naphthoic acid from naphthylmagnesium bromide and carbon dioxide but gives no experimental details regarding the process. According to Gilman and co-workers¹³ α -naphthylmagnesium bromide is formed only to the extent of 70% under optimum conditions. We have prepared α -naphthoic acid a great many times and found that the yields of crude acid, which had been washed free from inorganic salts and thoroughly dried, varied from 65–70% of the calculated amount.

Naphthylmagnesium bromide was prepared from 18 g. of magnesium, 156 g. of α -bromonaphthalene, 400 cc. of ether and a crystal of iodine. The oily Grignard reagent¹⁴ and the supernatant ether were poured into a 2-liter, wide-mouthed bottle the stopper of which was fitted with a stirrer, a wide carbon dioxide inlet tube which extended almost to the bottom of the bottle and a reflux condenser to which a calcium chloride tube was attached. During the reaction with carbon dioxide the bottle was immersed in ice water but the Grignard reagent should not be cooled before the addition of

¹² Acree, *Ber.*, 37, 627 (1904).

¹³ (a) Gilman and McCracken, *THIS JOURNAL*, 45, 2462 (1923); (b) Gilman and Parker, *ibid.*, 46, 2822 (1924).

¹⁴ This material tends to solidify readily if allowed to stand at ordinary temperature.

carbon dioxide or the naphthylmagnesium bromide will solidify to a hard cake which reacts very slowly with the gas. A brass rod, bent in a zig-zag form was found to be much more satisfactory than a stirrer made from glass. The Grignard reagent was stirred very vigorously and the gas, dried by passing it through three wash bottles filled with sulfuric acid, was led through it at a rapid rate. The reaction mixture became more and more viscous and at the end of one and one-half hours the mixture was decomposed in the usual manner. The naphthoic acid was extracted from the ether layer with dilute sodium carbonate solution.

If the ether suspension of naphthylmagnesium bromide was refluxed during the addition of carbon dioxide the yield of naphthoic acid was decreased to about 35% of the calculated amount.

Di- α -naphthyl Ketone.—For the preparation of large amounts of this ketone the method of Schmidlin and Massini¹⁵ is unsatisfactory, but we found that their method could be modified with advantage as follows. Naphthylmagnesium bromide, which had been freed from traces of unchanged magnesium by the subsequent addition of a small amount of α -bromonaphthalene, was added slowly, with stirring, to excess (2 equivalents) of cold naphthoyl chloride¹⁶ dissolved in ether. In this way the possible production of the tertiary carbinol was prevented to a considerable extent and the formation of the red impurity mentioned by Schmidlin and Massini was eliminated entirely. In spite of the fact that carefully purified materials had been used, the yield of pure ketone never exceeded 40% of the calculated amount. It was finally found that di- α -naphthyl ketone could be prepared easily, in large amounts, from the interaction of naphthylmagnesium bromide and naphthyl cyanide.

Naphthylmagnesium bromide (1.4 equivalents) was prepared in a liter flask from 45.5 cc. of α -bromonaphthalene, 7.5 g. of magnesium and 300 cc. of ether. Any unchanged magnesium was brought into solution by the subsequent addition of a few drops of bromonaphthalene. Thirty-three g. of naphthyl cyanide dissolved in ether was then added. Since the Grignard reagent had precipitated to a large extent in the form of a viscous oil, intimate contact of this substance with the cyanide was obtained by refluxing the mixture vigorously on a steam-bath. After a short time a granular precipitate began to form. The mixture was then heated for eight hours longer at a less vigorous rate. The ether, which contained binaphthyl, was decanted from the precipitate and the latter decomposed with ice and ammonium chloride. The ketone imine was extracted with ether, the solvent removed and the imine, in order to hydrolyze it to the ketone, was refluxed for twenty-four hours on a steam-bath with a mixture composed of 50 cc. of acetone, 100 cc. of water and 30 cc. of hydrochloric acid. After removal of the acetone by evaporation the granular product, which had been well washed with water, was dissolved in the least possible amount of hot alcohol. Upon cooling a brown oil was deposited. The alcoholic solution was decanted from this material and upon further cooling the ketone (23 g.) precipitated in crystalline form and in a quite pure state. The ketone was finally recrystallized from ether. From the brown oil, which soon solidified, a further amount (23 g.) of material was obtained which was recrystallized successively from acetic acid, alcohol and ether. The total yield of ketone was 75% of the calculated. Schmidlin and Massini¹⁵ state that di- α -naphthyl ketone, recrystallized from ether, is a colorless substance which melts at 103°. Tschitschibabin,⁷ who prepared the ketone by oxidation of the corresponding secondary carbinol, reported that the material, recrystallized from acetic acid, melted at 98°. We found that the ketone was often slightly yellow even after several recrystallizations

¹⁵ Ref. 6 a, p. 2388.

¹⁶ In order to prepare pure naphthoyl chloride, naphthoic acid was refluxed with 6 equivalents of thionyl chloride for two hours.

from ether and frequently yielded a deep yellow solution; in other instances the compound was obtained in a colorless condition after only one recrystallization and melted at 99–100°. The yellow color of the ketone is undoubtedly due to some impurity which is removed with difficulty.

α -Naphthoic Anhydride.—To a mixture of 4 g. of thoroughly dried, anhydrous sodium carbonate and 8 g. of naphthoyl chloride, there was added 2.5 cc. of pure pyridine. Apparently no reaction took place even when the mixture was warmed. However, upon the addition of a few drops of water to the cold mixture a vigorous reaction began. The mass was stirred thoroughly and then allowed to cool. After the addition of water the insoluble residue was dried and recrystallized from benzene. The compound melted at 145–146°. This anhydride had previously been prepared from calcium naphthoate and naphthoyl chloride.¹⁷ The yield of pure product was 5.3 g. or 80% of the calculated.

α -Naphthyl Cyanide.— α -Naphthoyl chloride was added to cold, concentrated ammonia water which was stirred vigorously and the acid amide formed was dried and then warmed gently for a short time with one equivalent of phosphorus pentachloride. The phosphorus oxychloride was removed by distillation; the residue was poured on ice, pulverized and thoroughly washed with water to remove phosphorus compounds. The crude cyanide was purified by distillation under ordinary pressure. The yield was practically quantitative.¹⁸

Di- α -naphthylcarbinol.—In the preparation of this carbinol according to the directions given in the literature,¹⁹ difficulty was encountered because of the formation of oily by-products; the use of excess ethyl formate seemed to be responsible for the formation of the oily material. Since naphthylmagnesium bromide can be obtained only in 70% yield,¹⁸ 0.7 of an equivalent of the ester (instead of 1 equivalent) should be used for 2 equivalents of the Grignard reagent. The Grignard reagent was prepared from 69 g. of bromonaphthalene, 7.2 g. of magnesium, 200 cc. of ether and a crystal of iodine. Seven and eight-tenths g. of freshly-distilled ethyl formate was added, a few drops at a time, during the course of half an hour and the mixture was thoroughly shaken and cooled after each addition of the ester. The carbinol, in the form of its magnesium bromide addition product, precipitated almost completely. After twenty-four hours the ether was decanted and the precipitate decomposed with ice and the calculated amount of dilute hydrochloric acid. The crystalline product was washed with a small amount of dilute hydrochloric acid, dried and then triturated with a small quantity of ether several times. The yield of pure product was 22 g.; m. p. 144°.

The carbinol can be converted easily into di- α -naphthylmethane as follows. Three g. of the carbinol was dissolved in 60 cc. of hot acetic acid and 25 g. of hydriodic acid (sp. gr. 1.96) was added to the hot solution, a small amount at a time. The mixture was then boiled for a few minutes. After twelve hours the methane, which had separated in the form of colorless needles, was filtered. The compound melted at 107–108° after recrystallization from alcohol.

Summary

It has been shown that under certain conditions triphenylmethyl is formed in the interaction of carbon dioxide and phenylmagnesium bromide.

¹⁷ Hofmann, *Ber.*, **1**, 42 (1868).

¹⁸ By a modification of the Sandmeyer synthesis of nitriles, Clarke and Read, *This Journal*, **46**, 1003 (1924), obtained a 55% yield of α -naphthonitrile from α -naphthylamine. West, *ibid.*, **42**, 1661 (1920), prepared the nitrile from sodium α -naphthalene sulfonate and potassium cyanide.

¹⁹ Ref. 6a, p. 2381; Tschitschibabin and Magidson, *J. prakt. Chem.*, **90**, 170 (1914).

Methods are given for the preparation of α -bromonaphthalene, α -naphthoic acid, di- α -naphthylketone and di- α -naphthylcarbinol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE POLARITY OF THE CARBON-HALOGEN BOND

I. DEVELOPMENT OF A QUANTITATIVE METHOD FOR THE DETERMINATION OF RELATIVE RATES FOR THE ACID HYDROLYSIS OF POSITIVE HALOGENS

BY JOHN R. SAMPEY

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Recently Nicolet and collaborators¹ have studied the different degrees of polarity that are shown by halogens attached to carbon in the aromatic series. The present investigation was undertaken with a two-fold purpose: to develop a more quantitative method for the determination of the rate of removal of positive halogens and to determine to what extent halogens in halogen naphthols show different degrees of polarity. The reaction which Nicolet has found useful as a preliminary test for positive halogens, that of the action of stannous chloride in acid solution on the organic halide, is one which has been applied in a qualitative way to the removal of halogen atoms from halogen amines and phenols² and to a less extent to the removal of bromine from bromo- β -naphthols and bromo- β -naphthylamines.³ The method described below differs from those referred to in that the hydrolysis was carried out in an oxygen-free atmosphere, and that the amount of halogen removed was determined by titration of the excess stannous chloride solution with standard iodine solution.⁴ It is thus considerably more convenient and rapid.

Method of Hydrolysis

The standard solution of stannous chloride was prepared by dissolving 60 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1000 g. of hydrochloric acid (37%) and the solution was diluted to 3700 cc. with 95% alcohol (the alcohol was added to make the organic halides soluble). This solution was stored in an atmosphere of hydrogen to prevent oxidation; after twenty-four hours the oxygen in the gases above the solution had disappeared and the stannous chloride maintained its strength unaltered during the time required to make the hydrolyses. The apparatus used for the storage of the solution and for the titration was

¹ (a) Nicolet, *THIS JOURNAL*, **43**, 2081 (1921); (b) Nicolet and Sampey, *ibid.*, **49**, 1796 (1927); (c) Nicolet and Ray, *ibid.*, **49**, 1801 (1927); (d) Nicolet and Sandin, *ibid.*, **49**, 1806 (1927); (e) Nicolet, *ibid.*, **49**, 1810 (1927).

² Burton and Kenner, *J. Chem. Soc.*, **121**, 675 (1922).

³ (a) Franzen, *J. prakt. Chem.*, **101**, 58 (1920); (b) **103**, 352 (1922); (c) Fries, *Ann.*, **334**, 342 (1904).

⁴ Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York City, 1919, p. 698.

similar to that described by Thornton.⁵ The standardization of the stannous chloride solution against a 0.1 *N* solution of iodine was done in an atmosphere of nitrogen.

Briefly, the procedure as finally adopted in the method of hydrolysis was as follows. A weighed sample of the organic halide was placed in an Erlenmeyer flask and, after sweeping out the air with a stream of nitrogen, an excess of the stannous chloride solution was introduced. The flask was placed under a reflux condenser in a thermostat heated to 70° and the temperature of the thermostat was kept constant within $\pm 0.01^\circ$. A layer of oil over the surface of the water in the thermostat prevented evaporation and made it easier to maintain a constant temperature. The solution was kept in an atmosphere of nitrogen at all times and at the end of a definite length of time the flask was removed from the thermostat to a pail of water where it was cooled for one minute. The amount of halogen removed from the organic halide by the hydrolysis was determined by titration of the excess of stannous chloride with 0.1 *N* iodine solution. The calculation of the amount of halogen removed was based on the number of cubic centimeters of stannous chloride solution consumed in the removal of all of the bromine and iodine from the halogen phenols and naphthols; as was expected, it was found that one mole of stannous chloride was required in every case for the complete removal of each atom of bromine or iodine; for example, exactly half a gram of 1-bromo-2-hydroxynaphthalene, when heated until all the bromine was removed, oxidized as much stannous chloride solution as did 43.80 cc. of 0.1 *N* iodine. This would be equivalent to the presence of 0.3504 g. of molecular bromine, but there are only 0.1750 g. of bromine in the 0.5 g. sample used. This is further evidence that the halogen when removed is positive.^{1a}

Several sources of error in the hydrolysis were examined. It was possible that some iodine substitution might have taken place during the titration with the standard iodine solution; no evidence of interaction of the iodine solution with the halogenated or unhalogenated phenols and naphthols was found when titrations were made. Care was taken to recrystallize several times all compounds used in order to free them from adsorbed halides and other impurities. A considerable error in the rate measurement was introduced by the method of heating the stannous chloride solution from room temperature to 70° after the introduction of the organic halide. Except in the cases of those compounds which lost their halogen rapidly, this error was found to be less than that caused by the entrance of atmospheric oxygen when attempts were made to introduce the halide into the stannous chloride solution after it had reached a constant temperature of 70°. It was not possible to remove portions of the solution from time to time for titrations without greatly increasing the difficulty of manipulation in keeping out the oxygen of the atmosphere. Efforts were made to keep the error introduced by the method of heating constant by the use of the same volume of stannous chloride solution in all the hydrolyses; in some cases this was not possible because of the insolubility of several of the compounds.⁶

⁵ Thornton, *THIS JOURNAL*, 43, 91 (1921).

⁶ In the next article it will be seen that the errors in the method of hydrolysis were further reduced by (a) heating the compounds which lose the halogens rapidly in a solution of lower hydrogen-ion concentration, (b) increasing the amount of alcohol for the highly insoluble compounds and (c) introducing the organic halide after the stannous chloride solution has reached 70°.

The results of the hydrolyses are summarized in the following table.

TABLE I
ACID HYDROLYSIS OF HALOGEN PHENOLS AND HALOGEN NAPHTHOLS

Compounds	Weight g.	Time of hydrolysis, min.	Cc. of SnCl ₄ soln. introduced	Cc. of 0.1 N iodine consumed in titrations	G. of halogen removed	Total halogen removed, %
1-Iodo-2-hydroxynaphthalene	0.5	5	20.00	11.20	0.1034	44.01
	.5	5	20.00	11.05	.1043	44.41
1-Bromo-2-hydroxynaphthalene	.5	15	20.00	21.00	.0260	14.85
	.5	15	20.00	21.20	.0252	14.40
1-Bromo-2-methoxynaphthalene	.3	90	20.00	26.90	.0024	2.37
1,6-Dibromo-2-hydroxynaphthalene	.5	60	40.00	47.00	.0320	12.12
	.5	60	40.00	46.80	.0328	12.42
2,4-Dibromo-1-hydroxynaphthalene	.5	60	40.00	49.90	.0204	7.72
	.5	60	40.00	50.10	.0196	7.42
1,4-Dibromo-2,3-dihydroxynaphthalene	.2	10	40.00	44.60	.0416	41.60
	.2	10	40.00	44.60	.0416	41.60
1,4,6,7-Tetrabromo-2,3-dihydroxynaphthalene	.1	10	40.00	50.50	.0180	26.89
	.1	10	40.00	50.58	.0176	26.38
4,6-Di-iodoresorcinol	.3	5	20.00	11.10	.1040	49.55
	.3	5	20.00	11.30	.1028	48.94
4,6-Dibromoresorcinol	.2	60	20.00	25.20	.0092	7.73
	.2	60	20.00	25.00	.0100	8.40
2,5-Dibromohydroquinone	.3	90	20.00	27.45
4,5-Dibromocatechol	.3	60	20.00	27.40
1,2-Dimethoxy-4,5-di-iodobenzene	.3	90	20.00	26.80	.0044	2.33
3,4,5,6-Tetrabromocatechol	.3	60	20.00	27.50
2,4-Dibromophenol	.3	60	20.00	27.45

Discussion of Table I

The most striking result shown in Table I is the remarkable reactivity of the halogen atoms in halogen naphthols. On the basis of the Lewis definition of a bond, the significance of the fact is that the bonding pair of electrons in the carbon-halogen bond of halogen naphthols is drawn further from the halogen nucleus and nearer the carbon than is the case with halogen phenols. Identification of the organic products of the reaction showed, however, that halogens in the 6 and 7 positions did not respond to the test for positive halogens, for they were not removed even on prolonged heating. 6-Bromo-2-hydroxynaphthalene was isolated after the reduction of the 1,6-dibromo-2-hydroxynaphthalene had gone as far as it would under the experimental conditions, and 6,7-dibromo-2,3-dihydroxynaphthalene was identified after the reduction of the tetra-bromo derivative. These results lend further support to the explanation^{1c} for the mechanism of the removal of positive halogens through quinone formation, for Vesely and Jokes⁷ have shown that of the six naphthoqui-

⁷ Vesely and Jokes, *Bull. soc. chim.*, 33, 955(1923).

nones of Willstätter, the two which are the most readily formed possess an intact benzene nucleus.

Preparation of Compounds

In the preparation of the compounds studied in Table I it was found necessary in several cases to modify the procedure as described in the literature. Attempts to prepare 2,3-dihydroxynaphthalene from "R-salt" by the method of Friedländer⁸ were so unsuccessful that considerable time was consumed in the development of a satisfactory method of preparation. When the reaction was carried out as described the chief product was β -naphthol. This indicated that the alkali fusion of the "R-salt" had failed to replace the 3-sulfonic acid group by an hydroxyl group and that the subsequent bomb reaction had removed both the 3- and 6-sulfonic acid groups. An increase in the temperature of the fusion resulted in considerable charring; varying the amount of water added to the fusion failed to produce the desired result. A potassium hydroxide fusion was substituted for the sodium hydroxide fusion and the temperature was raised to 300°; no water was added. When this fusion was acidified, much sulfur dioxide was liberated, indicating the removal of a sulfonic acid group. The bomb reaction proved that the 3-sulfonic acid group had been replaced with the hydroxyl group. The conditions under which the bombs were heated were also changed, for after more than twenty trials in which the temperature, the concentration of the sulfuric acid and the time of heating were varied, it was found that there was less charring when the strength of the acid was reduced from one-to-three to a concentration of one-to-four. This made it necessary to increase the time of heating to fourteen hours at 165–175°. The 2,3-dihydroxynaphthalene was brominated according to Fries.⁹ Attempts to prepare an iodo-derivative by direct iodination of the 2,3-dihydroxynaphthalene resulted in the formation of a dark, amorphous mass with the disappearance of little of the iodine.

Armstrong⁹ mentions the fact that 1,6-dibromo-2-hydroxynaphthalene can be prepared by bromination of β -naphthol in acetic acid; no details are given. The following procedure gave a yield of 90%: 25 g. of β -naphthol was dissolved in 150 cc. of acetic acid; to the solution was added slowly two moles (55.5 g.) of bromine in 35 cc. of acetic acid. The solution was heated almost to boiling for twenty minutes in order to expel the hydrogen bromide; it was cooled and water was added slowly to precipitate the dibromonaphthol. The solution was filtered and the product dried and recrystallized from hot alcohol.

In following out the procedure of Jackson¹⁰ for the preparation of tetrabromocatechol so much difficulty was experienced in keeping the products in solution during the bromination that a solvent other than chloroform was sought. When the bromination was made in acetic acid, there was no precipitation of the partially brominated products.

Summary

1. A quantitative method is described for the determination of relative rates of acid hydrolysis of positive halogens.
2. The test for positive halogens has been extended to halogen naphthols.
3. Improved methods of preparation are given for several halogen phenols and naphthols.

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⁸ Friedländer and Zakrzewski, *Ber.*, 27, 761 (1894).

⁹ Armstrong, *Ber.*, (2) 24, 705 (1891).

¹⁰ Jackson, *Am. Chem. Jour.*, 26, 31 (1901).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE POLARITY OF THE CARBON-HALOGEN BOND

II. THE KINETICS OF THE ACID HYDROLYSIS OF HALOGEN PHENOLS AND HALOGEN NAPHTHOLS

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The development of a quantitative method for the determination of relative rates of acid hydrolysis of positive halogens¹ has opened the way for a study of the kinetics of the reaction. In the present article an investigation is made on the effect of a change in both the hydrogen-ion concentration and the stannous chloride concentration upon the velocity of the reaction that has been used as a test for the determination of the degree of polarity of the halogen atoms in halogen phenols and halogen naphthols.

Effect of Hydrogen-Ion Concentration

The effect of a change in the hydrogen-ion concentration of the solution was first investigated. The total acidity of the stannous chloride solution used in Table I of the preceding article was determined by titration against a normal sodium hydroxide solution: 5.0 cc. of the stannous chloride solution neutralized 14.6 cc. of the normal sodium hydroxide. A solution of about one-seventh this total acidity was prepared by making up 50 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 80 g. of hydrochloric acid (37%) to 2960 cc. with 95% alcohol; 20.0 cc. of this solution neutralized 8.5 cc. of normal sodium hydroxide. The stronger acid solution removed 0.0260 g., or 14.85%, of the bromine from 1-bromo-2-hydroxynaphthalene in twenty minutes; the weaker acid solution removed 0.0072 g., or 4.1%, of the bromine in the same length of time.

It is not justifiable to draw any conclusions of a quantitative nature from these data on the relation between the hydrogen-ion concentration and the speed of the reaction, because the relation of the total acidity as determined to the actual hydrogen-ion concentration of the solutions is unknown. By taking advantage, however, of the qualitative relation, we were able to slow down the hydrolysis of the more positive halogen compounds found in Tables II, IV, VII and VIII, and to speed up the removal of the bromine from the less positive halogen compounds found in Tables III, V, VI and IX.

A possible mechanism for the acid hydrolysis of positive halogens has been formulated;² the role of the hydrogen ions in the reaction, however, is very likely catalytic. According to the theories of Lapworth³ and more

¹ Sampey, *THIS JOURNAL*, **49**, 2849 (1927).

² Nicolet, *ibid.*, **49**, 1810 (1927).

³ Lapworth, *J. Chem. Soc.*, **107**, 857 (1915).

recently Rice,⁴ it is the unhydrated hydrogen ions that catalyze reactions of this type. Experiments are planned to determine the effect of moisture on the rate of removal of the halogens by acids.

Effect of Stannous Chloride Concentration

The hydrolysis was further studied to determine the effect of a change in the concentration of the stannous chloride. In order to increase the acidity of the solution and at the same time not add so much water that half a gram of the organic halides would not dissolve readily, dry hydrogen chloride gas was passed into a solution containing 200 cc. of the 37% hydrochloric acid and two liters of 95% alcohol; 5.0 cc. of this solution neutralized 22.3 cc. of normal sodium hydroxide. This high concentration of acid caused more rapid hydrolysis. The following constants were obtained when the data were substituted in the equation for a first-order reaction: $1/t \times \log a/(a-x) = 0.4343k$, where a is the amount of removable bromine in the sample, and x is the amount of bromine removed.

TABLE I
HYDROLYSIS OF HALF-GRAM SAMPLES

1-Bromo-2-hydroxynaphthalene					
Time, min.	Cc. of SnCl ₂ ^a soln.	Cc. of 0.1 N I ₂ soln.	a	x	$k \times 10^{-1}$
5	20.00	15.93	0.1793	0.0203	2.39
10	20.00	10.82	.1793	.0432	2.52
15	20.00	6.49	.1793	.0580	2.60
18	20.00	5.27	.1793	.0629	2.39
20	20.00	3.80	.1793	.0688	2.41
					Mean 2.46
1,6-Dibromo-2-hydroxynaphthalene					
					$k \times 10^{-1}$
20	20.00	14.03	0.1324	0.0279	1.17
40	20.00	9.39	.1324	.0464	1.07
60	20.00	6.05	.1324	.0599	1.00
					Mean 1.08
2,4-Dibromo-1-hydroxynaphthalene					
					$k \times 10^{-1}$
40	20.00	15.25	0.2649	0.0230	2.26
50	20.00	14.10	.2649	.0276	2.19
60	20.00	11.95	.2649	.0362	2.44
					Mean 2.29

^a 20.00 cc. of this SnCl₂ solution was equivalent to 21.00 cc. of 0.1 N iodine.

The rate of removal of the halogens by the acid solution is apparently independent of the concentration of the stannous chloride; the evidence therefor is still more conclusive in Tables IV-IX below, where the range of concentration over which the reaction is studied is wider. Nicolet³ has used in his interpretation of the mechanism of the removal of positive

⁴ Rice, *THIS JOURNAL*, 45, 2808 (1923).

halogens this significant fact of the independence of the concentration of the stannous chloride on the rate of hydrolysis.

If we wish to determine how far, relatively, the bonding pair of electrons has been drawn from any positive halogen, it is more significant to use that weight of each compound which will lose the same weight of halogen on complete hydrolysis than it is to employ the same weight of each halogen phenol and naphthol. In the next two tables of data the halogen atoms that were not removed were not counted in when determining the equivalent weights to be used; for instance, 0.25 g. of 2,4-dibromo-1-hydroxynaphthalene was taken and 0.5 g. of 1,6-dibromo-2-hydroxynaphthalene, because in the latter only one bromine atom is removed. The weight of bromine lost on complete hydrolysis of 1,6-dibromo-2-hydroxynaphthalene was taken as the standard in the calculations for the amount of other halogens to be used. Due to the large differences in the rates of hydrolysis of the compounds, as shown in the preceding article of this series, it was necessary to prepare two stannous chloride solutions with different hydrogen-ion concentrations; the solution with the weaker hydrogen-ion concentration was used with those compounds whose halogens were more positive. The solution used in Table II was prepared by passing dry hydrogen chloride gas into 95% alcohol; 30 g. of SnCl_2 -

TABLE II
HYDROLYSIS OF EQUIVALENT QUANTITIES IN WEAK ACID

1-Bromo-2-hydroxynaphthalene						
Sample, g.	Time, min.	Cc. of SnCl_2^a soln.	Cc. of 0.1 N I_2 soln.	α	π	$k \times 10^3$
0.3690	20	30.00	18.15	0.1324	0.0185	7.46
.3690	30	30.00	16.10	.1324	.0267	7.46
.3690	45	30.00	13.40	.1324	.0375	7.38
						Mean 7.43
1-Iodo-2-hydroxynaphthalene						
0.2815	5	30.00	7.72	0.1324	0.0954	2.55
.2815	6.5	30.00	5.94	.1324	.1067	2.52
.2815	8	30.00	4.45	.1324	.1162	2.62
						Mean 2.56
1,4-Dibromo-2,3-dihydroxynaphthalene						
						$k \times 10^{-2}$
0.2631	12	30.00	13.00	0.1324	0.0390	2.90
.2631	16	30.00	9.90	.1324	.0514	3.06
.2631	20	30.00	8.70	.1324	.0562	2.76
						Mean 2.90
1,4,6,7-Tetrabromo-2,3-dihydroxynaphthalene						
						$k \times 10^{-3}$
0.3940	12	30.00	12.15	0.1324	0.0424	3.21
.3940	16	30.00	9.75	.1324	.0520	3.11
.3940	22	30.00	7.35	.1324	.0616	2.84
						Mean 3.05

* 30.00 cc. of this SnCl_2 solution was equivalent to 22.75 cc. of 0.1 N iodine.

2H₂O was added to the 2800 cc. of solution; 5.0 cc. of this solution neutralized 13.8 cc. of normal sodium hydroxide. For the solution used in Table III it was necessary to add about 300 g. of 37% hydrochloric acid along with the dry hydrogen chloride gas and alcohol in order to prevent the escape of hydrogen chloride fumes when the temperature was raised to 70 degrees (an alcoholic hydrogen chloride solution fumes at a lower concentration than an aqueous hydrogen chloride solution). Five cc. of this solution neutralized 21.9 cc. of normal sodium hydroxide. 1-Bromo-2-hydroxynaphthalene was hydrolyzed by both solutions in order to furnish a means for the comparison of the rates of the halogen removal in the two solutions.

TABLE III
HYDROLYSIS OF EQUIVALENT QUANTITIES IN STRONG ACID
1,6-Dibromo-2-hydroxynaphthalene

Sample, g.	Time, min.	Cc. of SnCl ₂ ^a soln.	Cc. of 0.1 N I ₂ soln.	<i>a</i>	<i>x</i>	<i>k</i> × 10 ⁻³
0.5000	30	30.00	10.00	0.1324	0.0160	4.28
.5000	45	30.00	7.85	0.1324	0.0246	4.56
.5000	60	30.00	6.40	0.1324	0.0304	4.34
						Mean 4.39
1-Bromo-2-hydroxynaphthalene						<i>k</i> × 10 ⁻³
0.3690	10	30.00	10.45	0.1324	0.0142	1.13
.3690	15	30.00	9.08	.1324	.0197	1.07
2,4-Dibromo-1-hydroxynaphthalene						<i>k</i> × 10 ⁻³
0.2500	60	30.00	10.46	0.1324	0.0142	1.88
4,6-Dibromoresorcinol						<i>k</i> × 10 ⁻³
0.2217	45	30.00	11.95	0.1324	0.0082	1.42
.2217	60	30.00	11.40	.1324	.0104	1.36
.2217	75	30.00	10.70	.1324	.0132	1.40
						Mean 1.36

^a 30.00 cc. of this solution was equivalent to 14.0 cc. of 0.1 N iodine.

By the use of equivalent quantities the interesting fact appears in Table II that the 1,4-bromine atoms in the two dihydroxynaphthalenes are removed at approximately the same rate; such a relation could not be drawn from any preceding results. In view of this relation, it is surprising to find in Table III that the bromine atom in the 6 position of 1,6-dibromo-2-hydroxynaphthalene exerts a decided influence upon the bromine in the 1 position.

In the final series of runs⁵ the effect of a wide range of concentration of the stannous chloride was determined. The method of hydrolysis was slightly changed: in each case 25.0 cc. of stannous chloride solution was

⁵ The results set forth in Tables IV-IX were obtained in the Chemical Laboratory of Howard College.

heated to the temperature of the thermostat before the organic halide was introduced. The oxygen of the atmosphere was kept out by keeping the tube from the cylinder of nitrogen below the neck of the Erlenmeyer flask when the sample was introduced. In order to control the rate of the hydrolysis a stannous chloride solution of different hydrogen-ion concentration was used for each compound; for the more positive halogens a solution of low acidity was used. The weight of organic halide used first in Tables IV-VI was sufficient to oxidize on complete hydrolysis 25.0 cc. of 0.1 *N* stannous chloride solution; in the last three tables that weight of sample was used which would oxidize all of the stannous chloride present on complete removal of the positive halogens. The solutions used in Tables IV-IX were made as follows.

Table IV: 160 g. of HCl (37%) and 14 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ made up to a volume of one liter with 95% alcohol.

Table V: 435 g. of HCl (37%) and 25 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 23.0 cc. of *N* NaOH.

Table VI: 175 g. of HCl (37%) and 15 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 10.4 cc. of *N* NaOH.

Table VII: 135 g. of HCl (37%) and 26 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 7.7 cc. of *N* NaOH.

Table VIII: 160 g. of H_2SO_4 (concentrated) and 30 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ made up to one liter with 95% alcohol; 200 cc. of water was added in an attempt to dissolve the heavy precipitate of tin salts; 5.0 cc. of this solution neutralized 12.6 cc. of *N* NaOH.

Table IX: 435 g. of H_2SO_4 (concentrated), 35 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 150 cc. of water were made up to a volume of one liter with 95% alcohol.

TABLE IV
HYDROLYSIS OF 1-iodo-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 <i>N</i> I_2^a soln.	α	π	$k \times 10^{-2}$
0.3359	10	19.6	0.1580	0.0596	4.73
.3359	15	16.0	.1580	.0826	4.92
.3359	20	13.4	.1580	.0989	4.92
.3359	30	9.5	.1580	.1237	5.09
.4738	10	14.9	.2229	.0894	5.13
.4738	15	10.3	.2229	.1186	5.13
.4738	20	6.8	.2229	.1408	4.97
.4738	30	1.4	.2229	.1751	5.13

^a 29.0 cc. of this 0.1 *N* iodine was equivalent to 25.0 cc. of SnCl_2 solution.

TABLE V
HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 <i>N</i> I_2^a soln.	α	π	$k \times 10^{-2}$
0.2787	10	33.0	0.1000	0.0340	4.15
.2787	15	30.2	.1000	.0452	4.01
.5574	10	25.2	.2000	.0652	3.94
.5574	15	20.7	.2000	.0832	3.58
.8361	10	18.7	.3000	.0912	3.60

^a 41.5 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of the SnCl_2 solution.

TABLE VI
HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 N I ₂ ^a soln.	σ	π	$k \times 10^{-3}$
0.2787	40	18.0	0.1000	0.0124	3.30
.2787	50	17.3	.1000	.0152	3.29
.5574	30	16.6	.2000	.0180	3.14
.5574	40	15.6	.2000	.0220	2.91

^a 21.1 cc. of this 0.1 N iodine solution oxidized 25.0 cc. of SnCl₂ solution.

TABLE VII
HYDROLYSIS OF 1-IDO-2-HYDROXYNAPHTHALENE

Sample g.	Time, min.	Cc. of 0.1 N I ₂ ^a soln.	σ	π	$k \times 10^{-3}$
0.5395	10	25.0	0.2538	0.0825	3.93
.5395	15	20.3	.2538	.1122	3.90
.5395	20	17.1	.2538	.1327	3.70
.5395	30	10.3	.2538	.1733	3.82
.5395	45	4.6	.2538	.2121	4.01
.2697	15	29.2	.1269	.0559	3.85
.8092	5	28.4	.3807	.0609	3.48
.8092	15	14.5	.3807	.1492	3.31

^a 38.0 cc. of this 0.1 N iodine solution oxidized 25.0 cc. of SnCl₂ solution.

TABLE VIII
HYDROLYSIS OF 4,6-DI-IODORESORCINOL

Sample, g.	Time, min.	Cc. of 0.1 N I ₂ ^a soln.	σ	π	$k \times 10^{-3}$
0.2260	15	16.1	0.1586	0.0527	2.69
.2260	30	10.0	.1586	.0914	2.90
.4520	12	11.4	.3172	.0825	2.51
.4520	20	4.8	.3172	.1244	2.49

^a 24.4 cc. of this 0.1 N iodine solution oxidized 25.0 cc. of SnCl₂ solution.

TABLE IX
HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 N I ₂ ^a soln.	σ	π	$k \times 10^{-3}$
0.4454	15	26.5	0.1598	0.0580	3.00
.4454	30	18.9	.1598	.0884	2.68
.2227	15	33.7	.0799	.0292	3.02
.2227	30	29.1	.0799	.0476	2.88

^a 41.0 cc. of this 0.1 N iodine solution oxidized 25.0 cc. of SnCl₂ solution.

Summary

1. The rate of removal of positive halogens from halogen phenols and halogen naphthols increases strikingly with the acid concentration.
2. The rate of hydrolysis in acid solution is independent of the concentration of the stannous chloride.

BIRMINGHAM, ALABAMA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, SOUTH DAKOTA STATE COLLEGE]

THE SOLUBILITY OF BARIUM *n*-BUTYRATE^{1,2}

BY HENRY J. WING

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In 1887 Sedlitzky³ determined the solubilities of the calcium salts of isovaleric, isobutyric and methylacetic acids. In 1902 Lumsden⁴ determined the solubilities of a number of calcium salts of the acetic acid series. In 1903 Walker and Fyffe⁵ studied the solubility of barium acetate. In 1926 the solubility of barium propionate was reported.⁶ Since some of these later determinations are at variance with those of the earlier investigators, the determination of the solubility of barium *n*-butyrate was undertaken, although it had been reported by Desz thy in 1893.⁷

While Desz thy's curve for the solubility of barium *n*-butyrate, as shown by the dotted line in Fig. 1, is somewhat similar to that obtained in this investigation, yet there is a distinct difference in the values obtained.

Experimental Part

Preparation of the Salt.—The barium *n*-butyrate was prepared by treating c. p. barium hydroxide with a slight excess of *n*-butyric acid (Eastman's, *n*-Butyric acid No. 60) and evaporating the solution to crystallization. The crystals were washed with alcohol and dried. The analyses in Table I show that the alcohol washing had no effect on the composition of the salt.

Determination of the Composition of the Hydrate.—Desz thy reported that the salt in contact with solution was the dihydrate over the entire temperature range.⁷

The salt crystallizes slowly from the solution in beautiful star-shaped clusters of slender crystals. Some individuals over two centimeters in length were obtained. As shown in Table I the salt is in the water-free form at 20° and washing with alcohol and drying at 60° have no effect on its composition. The analysis of the salt at 0° indicates that it is also anhydrous. A microscopic examination of these latter crystals showed them to be identical with those at 20°.

¹ This is the second of a series of determinations of the solubilities of the barium salts of the fatty acids.

² The early completion of this study was accomplished only by the assistance of one of our senior students, Mr. C. W. Eddy, which assistance it gives me great pleasure to acknowledge.

³ Sedlitzky, *Monatsh.*, **8**, 563 (1887).

⁴ Lumsden, *J. Chem. Soc.*, **81**, 350 (1902).

⁵ Walker and Fyffe, *ibid.*, **83**, 173 (1903).

⁶ Wing and Thompson, *THIS JOURNAL*, **48**, 104 (1926).

⁷ Desz thy, *Monatsh.*, **14**, 245 (1893).

TABLE I
DETERMINATION OF FORM OF SALT

Type of sample	Wt. of sample, g.	BaCrO ₄ found	BaCrO ₄ calcd. from Ba(but.) ₂	BaCrO ₄ calcd. from Ba(but.) ₂ .H ₂ O
Large crystals, H ₂ O washed, air dried at 20°	0.8609	0.6963	0.7003	0.6620
Small crystals, alc. washed, oven dried at 60°	.5500	.4452	.4474	.4229
Crystals at 20°, H ₂ O washed, air dried, 1 hour	.7737	.6205	.6294	.5950
Crystals at 0.3° for 60 hours, filtered and air dried, 1/2 hour	.5728	.5530	.5471	.5173

Determination of the Solubility.—The solubilities were determined by making up the solutions, with an excess of salt, in two large tubes. These were placed in a thermostat equipped with a thermo-regulator in which the mercury contact did not foul, although the current through the regulator was about one-half ampere.⁸ The regulation was within a 0.02° over the entire temperature range.

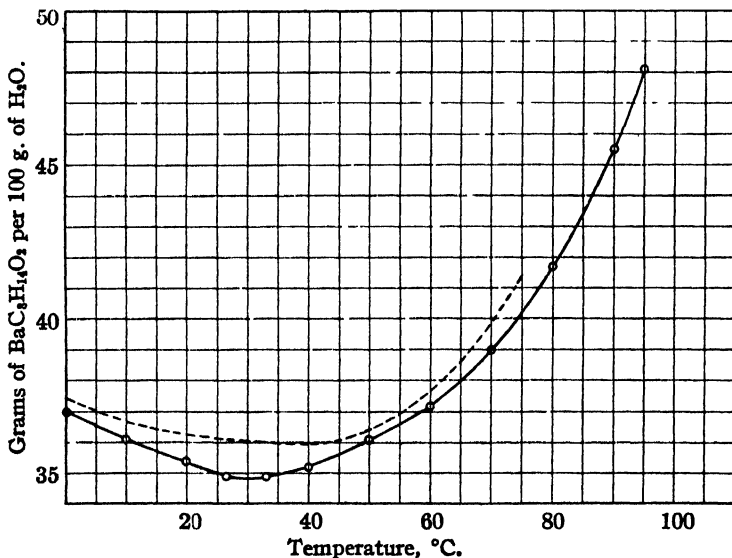


Fig. 1.

The solution in one tube was kept for half an hour at a temperature of from ten to twenty degrees above that of the observation and was then placed in the bath. The solution in the other tube was kept at a temperature below that of the observation until the experiment was ready to be carried out. The two solutions, placed in the bath at the required temperature, were stirred continuously for several hours, two to five, depend-

⁸ Wing and Thompson, *Ind. Eng. Chem.*, 17, 1242 (1925).

ing upon the temperature. Samples were then withdrawn by forcing the liquid through a filter and capillary tube into tared weighing bottles. The barium was precipitated in the form of the chromate and the amount of barium *n*-butyrate present was determined from this. Table II shows the results of these determinations and they are shown graphically by the solid line in Fig. 1.

The results of the determinations made by the supersaturation method and the undersaturation method were in very close agreement. In the average, the agreement was better than 0.2%. For example, by the undersaturation method, at 50.05° the test portion contained 26.50 g. of barium butyrate in 100 g. of solution, while at the same temperature, 26.53 g. of barium butyrate was found in 100 g. of solution by the supersaturation method. The values given in Table II are for the mean solubility at the various temperatures.

TABLE II
SOLUBILITY OF BARIUM BUTYRATE

Temp., °C.	0.06	9.92	19.86	26.50	33.00	39.98
Ba(but.) ₂ in 100 g. of soln., g.	27.0	26.5	26.1	25.9	25.9	26.0
Ba(but.) ₂ in 100 g. of water, g.	37.0	36.1	35.4	34.9	34.9	35.2
Temp., °C.	50.05	59.97	70.08	80.05	90.27	94.96
Ba(but.) ₂ in 100 g. of soln., g.	26.5	27.1	28.0	29.5	31.3	32.5
Ba(but.) ₂ in 100 g. of water, g.	36.1	37.2	39.0	41.7	45.5	48.1

Summary

1. The solubility of barium *n*-butyrate is a minimum at about 30°.
2. Over the entire temperature range, the salt in equilibrium with the solution is the water-free salt.
3. The solubility curve of barium *n*-butyrate is convex to the temperature axis.

BROOKINGS, SOUTH DAKOTA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

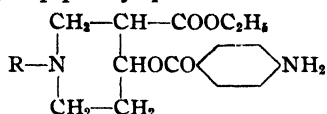
PIPERIDINE DERIVATIVES. V. THE PREPARATION AND REDUCTION OF CERTAIN PHENYL SUBSTITUTED 3-CARBETHOXY-4-PIPERIDONES. 1-CYCLOHEXYL- AND 1-PHENYLETHYL-3-CARBETHOXY-4-PIPERIDYL-PARA-AMINO BENZOATES¹

BY J. R. THAYER AND S. M. McELVAIN

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In an earlier communication by one of us² the preparation of a series of 1-alkyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoates of the formula

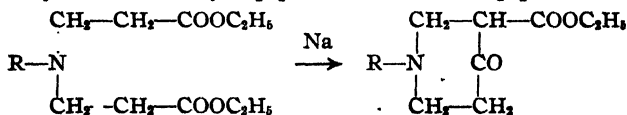


was described.

These substances showed very marked and unexpected physiological action. It was found that the size of the alkyl group in the 1 position had a pronounced effect on the physiological activity of the compounds, for, as the size of the alkyl group was increased, the subcutaneous toxicity was lowered and the efficiency for corneal anesthesia raised.

Because of this unexpected behavior, it seemed advisable to study the effect of substituting certain aryl and aryl-alkyl groups in the 1 position of the piperidine nucleus of the type compound shown above.

The preparation of such derivatives necessarily involved the synthesis of the corresponding piperidones by the same internal aceto-acetic ester condensation of the proper dicarbethoxy tertiary amines that was used for the 1-alkyl-3-carbethoxy-4-piperidones.³ The piperidones in which



R was the phenyl, benzyl and phenylethyl group were prepared. Very satisfactory yields (40–70%) of these piperidones were obtained, showing that the above condensation is of quite general application and is not materially affected by the nature of the R group.

The reduction of these phenyl substituted piperidones was interesting particularly as compared to the reduction of the 1-alkyl-3-carbethoxy 4-piperidones. When these latter compounds were reduced catalytically

¹ This paper is an abstract of a portion of the thesis submitted by J. R. Thayer to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry.

² McElvain, *This Journal*, **48**, 2239 (1926).

³ (a) McElvain, *ibid.*, **46**, 1721 (1924); (b) **48**, 2179 (1926).

with Adams' platinum-oxide platinum black catalyst it was found that 15-20 hours were required to reduce the ketone group to a point where it showed no coloration with ferric chloride. This reduction to a negative ferric chloride test generally required 10-20% excess of the theoretical amount of hydrogen necessary to convert the ketone into the secondary alcohol.

The 1-phenyl derivative, in the first three hours of the reduction, absorbed about 50% of the theoretical amount of hydrogen necessary to reduce both the ketone group and the benzene ring, and the reduction of the ketone group was not complete at this stage. The rate of reduction decreased somewhat after this rapid, initial absorption but at the end of twelve to fifteen hours the reduction was complete, as shown by the fact that approximately 15% excess of the hydrogen necessary to reduce both the ring and the ketone group had been absorbed and the reduction product gave no coloration with ferric chloride. Inasmuch as there was unreduced ketone present after hydrogen in excess of that required completely to reduce the ring had been absorbed, it is difficult to arrive at any conclusions as to the order in which the reduction took place. From the observations which were made, it may be that the ring and ketone group are reduced simultaneously, or that the ring was reduced before the reduction of the ketone began. In either case the final reduction product, as determined by derivatives, was 1-cyclohexyl-3-carbethoxy-4-hydroxypiperidine.

In the reduction of the 1-benzylpiperidone, there was no rapid initial absorption of hydrogen and both the ring and the ketone group seemed to reduce simultaneously. The reduction to a negative ferric chloride test took place in about 24 hours and required 65-75% of the theoretical amount of hydrogen necessary for the complete reduction of both the ring and ketone group. From this point the reduction was very slow but could be continued to a stage where an excess of 12-15% of the theoretical amount of hydrogen necessary to reduce both groups had been absorbed. It was not possible to isolate a crystalline derivative of the reduction product, either at the point where the ketone was completely reduced or at the point where more than sufficient hydrogen had been absorbed to reduce both the ketone and the ring. From the standpoint of producing a definite final product, the catalytic reduction of the 1-benzyl-3-carbethoxy-4-piperidone was unsuccessful, but it did show the effect of the separation of the aromatic nucleus from the amino nitrogen on the rate of nuclear hydrogenation.

In the case of the 1-phenylethyl-3-carbethoxy-4-piperidone, in which the aromatic nucleus is two carbon atoms removed from the amino nitrogen, the reduction proceeded in much the same manner as that of the 1-alkyl-3-carbethoxy-4-piperidones. A negative test for the ketone was obtained with ferric chloride after 10-12 hours of reduction and at this

point approximately 20% excess of the hydrogen necessary for the reduction of the ketone group had been absorbed. Thereafter there was practically no absorption of hydrogen even on prolonged exposure to reduction. As mentioned above, the 1-alkyl-3-carbethoxy-4-piperidones generally absorbed an excess of 10-20% of the hydrogen necessary for the reduction of the ketone to the secondary alcohol. From such data it is apparent that the reduction of the aromatic nucleus in the 1-phenylethylpiperidone does not take place to any marked extent, if at all.

The reduction products of these piperidones were acylated with *p*-nitrobenzoyl chloride. The derivative obtained from the 1-phenyl-3-carbethoxy-4-piperidone was assumed to be 1-cyclohexyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoate on account of (1) the amount of hydrogen absorbed during the reduction of the piperidone and (2) the absence of unsaturation in the *p*-nitrobenzoate as shown by dilute potassium permanganate solution.

It was not possible to isolate a crystalline *p*-nitrobenzoate from the acylation of the reduction product of the 1-benzylpiperidone. This reduction product showed a distinctly different behavior from the others with *p*-nitrobenzoyl chloride. There was very little evolution of hydrogen chloride when the reactants were heated together. Under the same conditions, the reduction products of the other piperidones gave a vigorous evolution of hydrogen chloride with *p*-nitrobenzoyl chloride. Such behavior would indicate that considerable reduction of the secondary alcohol group to a methylene group had taken place.

1-Phenylethyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoate was shown to be the derivative obtained from the acylation of the reduction product of the 1-phenylethyl-3-carbethoxy-4-piperidone by (1) the amount of hydrogen absorbed in the reduction of the piperidone and (2) the fact that benzoic acid was obtained by the oxidation of the reduction product.

The 1-cyclohexyl- and 1-phenylethyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoates were converted by catalytic reduction into the corresponding *p*-aminobenzoates, which were isolated as the crystalline dihydrochlorides

Experimental

β -Carbethoxyethylphenylamine.—This substance has been prepared by Harrie and Loth⁴ from aniline and β -iodopropionate. The following procedure was used in this work. A mixture of 180 g. (1 mole) of ethyl- β -bromopropionate and 190 g. (2 moles) of freshly distilled aniline was heated to 70-80° in an oil-bath with stirring. At this temperature a rather vigorous reaction took place, whereupon the heating was discontinued until this initial reaction had subsided. The mixture was then heated at 110-120° for two to three hours, after which it was cooled and the precipitated anilin hydrobromide filtered off by suction. The precipitate was washed with 200 cc. of ether. The ether was evaporated from the filtrate and the secondary amine distilled unde

⁴ Harries and Loth, *Ber.*, 29, 514 (1896).

diminished pressure. The yield was 140–145 g. (72–75% of the theoretical); b. p. 133–135° (2 mm.); n_D^{20} 1.5315; d_{20}^{20} 1.0709. The hydrochloride melted at 98–99°.

Anal. (of the hydrochloride). Subs., 0.2020: AgCl, 0.1261. Calcd. for $C_{11}H_{16}O_2 \cdot NCl$: Cl, 15.46. Found: 15.44 (of the free base).

Subs., 0.7972, 0.7169: 43.2, 40.4 cc. of 0.0911 *N* HCl. Calcd. for $C_{11}H_{16}O_2 \cdot N$: N, 7.25. Found: 6.91, 7.12.

β -Carbethoxyethylbenzylamine.—To a solution of 54 g. of benzylamine in 400 cc. of alcohol was added 90 g. (0.5 mole) of ethyl β -bromopropionate at such a rate that the temperature of the mixture did not exceed 50°. The mixture was then allowed to stand for about three hours. During this time it was shaken occasionally. Sixty g. of silver oxide was then added and the mixture shaken intermittently for two hours. The alcoholic solution of the amine was filtered with suction and the precipitate washed with 125–150 cc. of alcohol. The alcohol was removed from the filtrate by distillation and the amine dissolved in 400 cc. of ether. The ethereal solution was washed twice with 10% potassium cyanide solution, after which the solvent was removed and the amine distilled under diminished pressure. The yield was 63–68 g. (60–65% of the theoretical); b. p. 132–134° (2 mm.); n_D^{20} 1.5059; d_{20}^{20} 1.9126. The hydrochloride melted at 147–149°.

Anal. (free base). Subs., 1.1128, 1.2086: 56.77, 62.90 cc. of 0.0911 *N* HCl. Calcd. for $C_{12}H_{17}O_2 \cdot N$: N, 6.76. Found: 6.51, 6.64.

(Hydrochloride). Subs., 0.2700: AgCl, 0.1551. Calcd. for $C_{12}H_{17}O_2 \cdot NCl$: 14.58. Found: 14.20.

β -Carbethoxyethylphenylethylamine.—This amine was prepared in exactly the same manner as that described above for β -carbethoxyethylbenzylamine. The yields were 68–72 g. (62–65% of the theoretical); b. p. 145–147° (2 mm.); n_D^{20} 1.5040; d_{20}^{20} 1.0098. The hydrochloride melted at 161–163°.

Anal. (free base). Subs., 0.9994, 0.7326: 46.8, 36.3 cc. of 0.0911 *N* HCl. Calcd. for $C_{13}H_{19}O_2 \cdot N$: N, 6.33. Found: 5.97, 6.32.

(Hydrochloride). Subs., 0.2310: AgCl, 0.1277. Calcd. for $C_{13}H_{19}O_2 \cdot NCl$: Cl, 13.78. Found: 13.66.

β,β' -Dicarbethoxydiethylphenylamine.—A mixture of 195 g. (1 mole) of β -carbethoxyethylphenylamine and 90 g. (0.5 mole) of ethyl β -bromopropionate was heated at 110–120° for 36–40 hours. The reaction mixture was then treated with alkali solution and the free amines were extracted with three 200cc. portions of ether. The ether was removed by distillation and the amines were fractionally distilled under diminished pressure, the fraction boiling at 180–200° (2 mm.) being collected as the tertiary amine. The yield was 126–135 g. For analyses and physical constants this amine was further purified by shaking with an alkaline aqueous suspension of benzoyl chloride. On redistillation, the tertiary amine boiled at 182–184° (2 mm.); n_D^{20} 1.5176; d_{20}^{20} 1.0948.

Anal. Subs., 1.0248, 1.0295: 36.76, 37.47 cc. of 0.091 *N* HCl. Calcd. for $C_{16}H_{23} \cdot O_2N$: N, 4.78. Found: 4.58, 4.64.

β,β' -Dicarbethoxydiethylbenzylamine.—To 104 g. (0.5 mole) of β -carbethoxyethylbenzylamine in 100 cc. of alcohol was added 90 g. (0.5 mole) of ethyl β -bromopropionate. The mixture was allowed to stand for two and a half to three hours with occasional shaking and then heated to 100° for a half hour. The mixture was cooled to 20–30° and diluted with 300 cc. of alcohol. Sixty g. of silver oxide was then added and the mixture shaken intermittently for about two hours. The silver bromide was filtered off and the precipitate washed with 150 cc. of alcohol. The alcohol was removed from the filtrate, the amine dissolved in 400 cc. of ether and the ethereal solution washed twice with a dilute solution of potassium cyanide. After the removal of the ether the

amine was distilled under diminished pressure. The yield amounted to 92–95 g. (82–85% of the theoretical). The tertiary amine was freed from any secondary amine by treatment with benzoyl chloride. It then boiled at 181–183° (2 mm.); n_D^{20} 1.4942; d_{20}^{20} 1.0598.

Anal. Subs., 1.3649, 1.3025: 49.1, 46.5 cc. of 0.0911 *N* HCl. Calcd. for $C_{17}H_{23}O_4N$: N, 4.57. Found: 4.58, 4.56.

β,β' -Dicarbethoxydiethylphenylethylamine.—This amine was prepared according to the procedure given above for β,β' -dicarbethoxydiethylbenzylamine. The yield was 80–84 g. (50–52% of the theoretical); b. p. 190–193° (2 mm.); n_D^{20} 1.4990; d_{20}^{20} 1.0454.

Anal. Subs., 1.2533, 1.2248: 43.37, 40.80 cc. of 0.0911 *N* HCl. Calcd. for $C_{18}H_{17}O_4N$: N, 4.36. Found: 4.42, 4.25.

1-Phenyl-, 1-Benzyl- and 1-Phenylethyl-3-carbethoxy-4-piperidone Hydrochlorides.—These substances were prepared by the internal condensation of the corresponding dicarbethoxy tertiary amines with sodium in xylene and isolated by the procedure described by McElvain.^{3b}

TABLE I

1-Substituent	Formula	M. p., °C.	Yield, %	Analyses (%Cl) calcd.	found
Phenyl	$C_{14}H_{18}O_3NCl$	144–145	70	12.54	12.50
Benzyl	$C_{15}H_{20}O_3NCl$	170–172	50	11.93	11.84
Phenylethyl	$C_{16}H_{22}O_3NCl$	165–167	40	11.42	11.45

Reduction of 1-Phenyl-3-carbethoxy-4-piperidone Hydrochloride.—A solution of 20 g. of the piperidone in 125 cc. of alcohol was reduced catalytically using 0.5 g. of Adams' platinum-oxide platinum black catalyst, at room temperature and under a pressure of 2.5–3.5 atmospheres. The reduction of the ketone group was followed by testing portions of the solution for coloration with ferric chloride, and the reduction of the aromatic nucleus was estimated from the amount of hydrogen absorbed. Four molecular equivalents of hydrogen were necessary for the reduction of both the ketone group and the ring. In the first three hours of reduction approximately 2 molecular equivalents of hydrogen were absorbed. The absorption of hydrogen at the end of twelve hours amounted to 4.31 molecular equivalents, which was in excess of that theoretically necessary to reduce both groups. At this point a positive test for the ketone was obtained with ferric chloride. For complete reduction of the ketone it was necessary to continue the reduction for an additional six to eight hours, at the end of which time the ferric chloride test was negative and the total absorbed hydrogen amounted to 4.46 molecular equivalents. No attempt was made to isolate or purify the reduction product.

Reduction of 1-Benzyl-3-carbethoxy-4-piperidone Hydrochloride.—Twenty g. of this piperidone was reduced catalytically in the manner described above. In the first nine hours of reduction there was an absorption of 1.80 molecular equivalents of hydrogen and the ketone group was not completely reduced. In a series of six runs the minimum absorption of hydrogen necessary for the complete reduction of the ketone group was 2.51 molecular equivalents, while in the other cases it varied between 2.59 and 2.81 molecular equivalents. At the end of thirty-six to forty hours of exposure to reduction the amount of hydrogen absorbed amounted to 4.29–4.44 molecular equivalents.

Reduction of 1-Phenylethyl-3-carbethoxy-4-piperidone Hydrochloride.—The reduction procedure was the same as that outlined above for the 1-phenyl derivative. In the first twelve hours of reduction the amount of hydrogen absorbed was 1.49 molecular equivalents. This amount was approximately a 50% excess over that necessary for the ketone reduction. Upon exposure to reduction for an additional twenty-four

hours, there was practically no further absorption of hydrogen. This reduction product, after the removal of the solvent, yielded benzoic acid when oxidized with an aqueous potassium permanganate solution.

1-Cyclohexyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoate Hydrochloride.—The catalyst was filtered from the solution of the reduction product of the 1-phenyl-3-carbethoxy-4-piperidone and the alcohol removed by distillation under diminished pressure. After the complete removal of the solvent, 25 g. of *p*-nitrobenzoyl chloride was added and the mixture heated at 140–145° in an oil-bath until the evolution of hydrogen chloride ceased. The nitro ester was isolated by the same procedure as that used for the corresponding 1-alkyl compounds. The yield was 8–9 g. An aqueous solution of the hydrochloride of this *p*-nitrobenzoate gave no indication of unsaturation when treated with dilute aqueous potassium permanganate. The recrystallized *p*-nitrobenzoate hydrochloride melted at 188–190°.

Anal. Subs., 0.2530: AgCl, 0.0819. Calcd. for $C_{21}H_{27}O_6N_2Cl$: Cl, 8.05. Found: 8.00.

Attempted Acylation of the Reduction Product of 1-Benzyl-3-carbethoxy-4-piperidone Hydrochloride.—Several attempts were made to acylate the reduction product obtained when the reduction was stopped at the point where a negative test for the ketone was indicated. This product gave very little reaction with *p*-nitrobenzoyl chloride. The reduction product obtained when the reduction was continued to the point where an excess of hydrogen over that required to reduce both the ketone group and the ring had been absorbed, was treated with *p*-nitrobenzoyl chloride. In this case also there was very little evolution of hydrogen chloride. From neither of these attempted acylations was it possible to obtain a crystalline derivative of the reduction products. The lack of reaction with *p*-nitrobenzoyl chloride would indicate, it seems, that the ketone group had been converted, to a very large extent, to a methylene group.

1-Phenylethyl-3-carbethoxy-4-piperidyl-*p*-nitrobenzoate Hydrochloride.—The reduction product from the 1-phenylethyl-3-carbethoxy-4-piperidone, after the removal of the solvent, was treated with *p*-nitrobenzoyl chloride under the conditions described above. The reaction appeared to proceed normally and produced a copious evolution of hydrogen chloride. The hydrochloride of the *p*-nitrobenzoate crystallized well and behaved in all respects like the corresponding 1-alkyl derivatives. The yield was 15 g. of a product melting at 195–197°.

Anal. Subs., 0.2570: AgCl, 0.0805. Calcd. for $C_{23}H_{27}O_6N_2Cl$: Cl, 7.67. Found: 7.75.

1-Cyclohexyl- and 1-Phenylethyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoate Dihydrochlorides.—Ten g. of the *p*-nitrobenzoate hydrochloride was dissolved in 250 cc. of absolute alcohol and reduced catalytically using 0.25 g. of Adams' platinum-oxide platinum black catalyst. The reduction was complete in twenty to thirty minutes and the *p*-aminobenzoates were isolated as the dihydrochlorides by the procedure that was used for the 1-alkyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoate dihydrochlorides.²

TABLE II

1-Substituent	Formula	M. p., °C.	Analyses (% Cl)	
			Calcd.	Found
Cyclohexyl	$C_{21}H_{27}O_4N_2Cl_2$	220–222	15.85	15.47
Phenylethyl	$C_{23}H_{29}O_4N_2Cl_2$	215–218	15.12	14.85

Pharmacological Report

The authors are indebted to Mr. Charles L. Rose of the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana, for this

pharmacological report on the 1-cyclohexyl- and 1-phenylethyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoates.

The anesthetic efficiencies were tested by application of 1% solutions of the anesthetics ($P_H = 5$) to the rabbit's cornea and noting the duration of anesthesia. The toxicities were measured by subcutaneous injection into white mice. These data, together with comparative values for cocaine, are summarized in Table III.

TABLE III
PHARMACOLOGICAL DATA

1-Substituent	Duration of anesthesia in minutes with 1% solution (aver. for 5 rabbits)	Toxicity to white mice mg. per kg.	
		M. T. D.	M. L. D.
Cyclohexyl	26.1	100	150 (28 mice used)
Phenylethyl	46.4	1150	1200 (40 mice used)
Cocaine	20.4	200	250

The above data indicate that the 1-cyclohexyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoate is somewhat more efficient than cocaine in producing corneal anesthesia, while the corresponding 1-phenylethyl derivative is over twice as efficient as cocaine. The toxicity of the cyclohexyl derivative is slightly greater than that of cocaine, while the toxicity of the 1-phenylethyl derivative is approximately one-fifth that of cocaine.

The toxicity of the cyclohexyl derivative is interesting when compared with the corresponding 1-alkyl derivatives. In the case of these latter compounds it was found that the subcutaneous toxicity to white mice decreased as the size of the alkyl group in the 1 position was increased. The 1-methyl and 1-*iso*-amyl derivatives had values of 100 mg. per kg. and 550 mg. per kg., respectively, as the minimum lethal doses for white mice. It is seen from Table III that the 1-cyclohexyl derivative is approximately equivalent to the 1-methyl derivative in toxicity. It might have been expected that the presence of a group of such a carbon content as the cyclohexyl group in the 1 position would have produced a physiological effect of the order of that shown by the higher alkyl radicals, such as the *iso*-amyl radical. Since this expected similarity in behavior between the cyclohexyl group and the higher alkyl groups was not found to exist, it appears that the abnormal action of the former is due to its cyclic structure. The toxicity of the phenylethyl derivative is exceptionally low and, since at the same time its anesthetic efficiency is quite high, it indicates that phenyl-alkyl radicals may be very desirable N-substituent groups in local anesthetics.

Summary

1. The preparation of some 1,3,4-tri-substituted piperidines and the reduction of the corresponding 4-piperidones have been described.
2. A preliminary pharmacological report on the 1-cyclohexyl- and

1-phenylethyl-3-carbethoxy-4-piperidyl-*p*-aminobenzoates has been included.

3. This pharmacological report indicates that the cyclohexyl group does not correspond to the higher alkyl groups in its physiological effect and is a much less desirable N-substituent group than the phenylethyl group for this particular type of local anesthetic.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

AZO DYES CONTAINING ANTIMONY. II

By FITZGERALD DUNNING AND E. EMMET REID

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In a previous paper,¹ the preparation of a series of azo dyes containing antimony has been described. These compounds were prepared for a study of their possible therapeutic action. Since that time another series of dyes and several miscellaneous antimonials have been prepared. These compounds have been tested as to their activity against trypanosomes and as to their toxicities. The pharmacological findings, which are summarized here, will be published more fully elsewhere.

As these compounds are, for the most part, dyes, it was thought of interest to ascertain the effect of the antimony group on the color. Dyes containing the group $\text{—SbO}_3\text{H}_2$ have been contrasted with those having the SO_3H group and with some containing neither.

Results

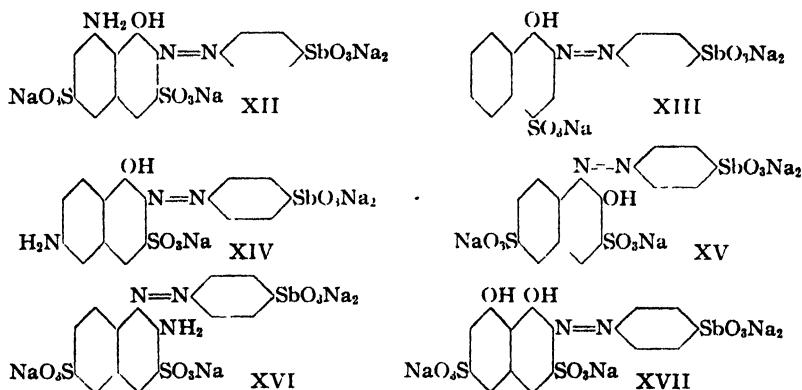
The compounds which have been prepared are for the most part derivatives of stibanilic acid, *p*-aminophenylstibinic acid $\text{—H}_2\text{NC}_6\text{H}_4\text{SbO}_3\text{H}_2$. The method of preparation of this compound has been further improved. This consists in breaking down the molecular compound formed by diazotized *p*-amino-acetanilide and antimony trichloride with hot sodium hydroxide. Thus stibanilic acid is obtained from the molecular compound in one step.

The first series of compounds, Nos. I to VI, described in the previous paper, were obtained by coupling diazotized stibanilic acids with substituted phenols. In the second series, diazotized stibanilic acid has been coupled with dimethyl- and diethylaniline to form *p*-dimethylamino-azobenzene-4'-stibinic acid and the corresponding diethyl compound (Nos. VII and VIII). The disodium salts, $\text{Na}_2\text{O}_3\text{SbC}_6\text{H}_4\text{N:N:C}_6\text{H}_4\text{N(R)}_2$, are normally formed and are readily soluble in water. The solutions are comparatively stable.

The third series has been prepared by coupling diazotized stibanilic acid with various substituted naphthalene sulfonic acids.

¹ Dunning and Reid, *THIS JOURNAL*, **48**, 2959 (1926).

The intermediates used were as follows: 1,8-naphthylamine-3,6-disulfonic acid (H-acid); 1-naphthol-4-sulfonic acid (Neville and Winther's acid); 5,2-naphthylamine-7-sulfonic acid (J-acid); 2-naphthol-3,6-disulfonic acid (R-salt); 2-naphthylamine-3,6-disulfonic (amino R salt); 1,8-dinaphthol-3,6-disulfonic acid (chromotrope), to form compounds XII, XIII, XIV, XV, XVI and XVII, respectively. The structural formulas are



Methylantranilate, *p*-aminodimethylaniline and benzidine have also been diazotized, coupled with antimony trichloride and treated with sodium hydroxide to give the following compounds: methyl *o*-stibono-benzoate, *p*-dimethylaminophenylstibinic acid and *p,p'*-dibenzenestibinic acid.

The sodium salts of all the compounds described have been tested as to their effectiveness against trypanosomiasis. For this purpose the white (albino) rat infected with *Trypanosoma equiperdum* has been used. All of the compounds of the first and second series have proved to be totally ineffective. With the third series, however, positive results have been obtained. Compound XII (as indicated above) has proved to be the most effective and compounds XVI and XIV follow in order.

The compounds which have been found to be effective possess approximately the same structural formulas, as the pharmacological table of findings will show. The presence of one amino group and one sulfonic acid group, and preferably two sulfonic acid groups, in the naphthalene intermediate, seems to be necessary, as an inspection of the formulas of compounds XII, XIV and XVI will show. These findings are in keeping with the conclusions of Ehrlich² and of Nicolle and Mesnil³ working with benzidine dyes.

That antimony is necessary is witnessed by the fact that analogous dyes made from sulfanilic acid have no trypanocidal action.

² Ehrlich, *Berl. klin. Wochschr.*, **44**, 233, 280, 310, 341 (1907).

³ Nicolle and Mesnil, *Ann. inst. Pasteur*, **20**, 417, 513 (1906).

Experimental

In following any of the general methods^{4,5} for the preparation of stibanilic acid, several difficulties are encountered.

Not only is the material hard to handle mechanically, but the yields are generally low. In the first place, on treating the diazotized amine solution with antimony trichloride, the oxychloride of antimony precipitates out unless the solution is strongly acid. When a strong sodium hydroxide solution of antimony oxide is used, the oxide precipitates. The greatest difficulty, however, is caused by the production of a stiff foam which prevents thorough mixing of the reactants and causes much trouble mechanically. This foam subsides only after standing for a considerable length of time (24 hours) and occasions much decomposition. To overcome this, we experimented with various foam-breakers such as ether, alcohol, acetone, etc., but these all seemed to cause decomposition and were discarded. We have developed, however, two methods which have proved fairly successful. One, a modification of the method of Schmidt, was reported previously. The other is shorter, in that two steps are combined.

A mixture of *p*-amino-acetanilide (150 g.), recrystallized after boiling with charcoal, and antimony trioxide (145 g.) in one liter of water containing sufficient 33% hydrochloric acid to dissolve the trioxide (600 cc.) was warmed until everything dissolved. On cooling, white crystals of the hydrochloride of the amine separated out. This mixture was cooled to 0° and diazotized with a solution of 69 g. of sodium nitrite in 460 cc. of water. The nitrite solution was introduced through a capillary at the bottom of the beaker, with mechanical stirring. During this slow addition a yellow, crystalline (rectangular plates) compound formed. This is the double salt of the type described by May.⁶

These diazonium chloride antimony trichloride complex salts are very stable and their formation is almost quantitative. As the product formed here, $\text{CH}_3\text{CONHC}_6\text{H}_4\text{-N}_2\text{Cl}\cdot\text{SbCl}_3$, is somewhat soluble in hydrochloric acid, the yield of this reaction is only about 90%.

This compound was filtered off, suspended in water and the suspension was added slowly to a 10% solution of sodium hydroxide heated to 90°, the solution being stirred mechanically. This method gave good results and the time of the procedure was considerably shortened. The evolution of nitrogen was comparatively rapid and the foam formed on each addition of the molecular compound subsided rapidly. The addition usually takes from one to two hours. After all the suspension was added, the solution was heated at the same temperature until a test filtered portion precipitated and redissolved in excess dilute hydrochloric acid. The solution was then nearly neutralized and saturated with carbon dioxide to precipitate impurities. It was filtered, and from the filtrate stibanilic acid, $\text{NH}_2\text{C}_6\text{H}_4\text{SbO}_2\text{H}_2$, precipitated by acetic acid, the acetyl group having been removed during the procedure. The crude stibanilic acid is removed from the liquid by centrifuging and is then ready for use. The yield varies but is generally about 50%, figured on the crude acid.

The breaking down of the molecular compound was also effected by ammonium hydroxide, sodium carbonate solutions and solutions of sodium hydroxide of varying strengths. The effect of copper powder, mild oxidizing agents, etc., was also tried with no success.

As the crude product has been found to be sufficiently pure for our purpose, it has been used without further purification. This has been

⁴ Ger. pat. 254,421 (1912); 261,825 (1913); 220,488 (1913).

⁵ Schmidt, *Ann.*, **421**, 174 (1920).

⁶ May, *J. Chem. Soc.*, **101**, 1037 (1912).

particularly fortunate as stibanilic acid is far from being a stable compound, decomposing rapidly on keeping. For this reason, we have prepared our acid as we needed it and have made no attempt to keep it in solid form.

Preparation of Dyes

The second and third series of dyes were made after the same general method described previously.¹ For the preparation of the second series, substituted anilines were utilized as intermediates. Dimethyl-, diethyl-, dipropyl- and dibutylaniline were used but, unfortunately, compounds were formed only by dimethyl- and diethylaniline. These were made as follows.

A calculated amount of stibanilic acid was diazotized with 10% sodium nitrite solution in the customary manner. This was poured into hydrochloric acid solutions containing calculated quantities of dimethyl- and diethylaniline. These solutions were allowed to stand for some time, filtered and made alkaline. The alkaline solutions were clear at first but on standing precipitates formed. These proved to be the *p*-nitroso derivatives of the substituted anilines used. Their formation is due to an excess of nitrous acid in the diazotized stibanilic acid solution, which is difficult to avoid. The solutions were filtered from these impurities and the acid dyes were precipitated by hydrochloric acid. These precipitates were collected by centrifuging and were dried and then washed with hydrochloric acid to remove any phenylstibinic acid or similar by-product and any excess of the intermediate.

The resulting *p*-dimethyl- (VII) and *p*-diethylamino-azobenzene (VIII) were, respectively, dull brown and dull purple in color and both were insoluble in water and organic solvents and soluble in sodium and ammonium hydroxide.

Anal. Calcd. for $C_{14}H_{16}O_2N_2Sb$: Sb, 30.7. Found: 29.9.

Calcd. for $C_{16}H_{20}O_2N_2Sb$: Sb, 28.7. Found: 27.5.

The third series of dyes has been prepared after the following general scheme. Calculated amounts of diazotized stibanilic acid were added to slightly alkaline solutions of various substituted naphthalene sulfonic acids in theoretical amounts. These solutions were warmed and allowed to stand for several hours and then filtered. The filtered solutions were evaporated to small volume on a water-bath. At this point the procedure of preparation differed according to the nature of the dye. If it was possible to precipitate by acid, the solution was acidified, the precipitate collected by centrifuging and dried. The dried, powdered precipitate was thoroughly washed with hydrochloric acid and then with water. This removed any excess intermediate or breakdown products of stibanilic acid. It was again dried and analyzed for antimony. The following compounds were prepared by this method.

Diazotized stibanilic acid was coupled with Neville and Winther's acid, J-acid and amino R salt, respectively, to give compound XIII, dark red; compound XIV, light red brown; and compound XVI, dark brown. Compounds XIII and XIV were insoluble in water. Compound XVI was moderately soluble. All were insoluble in organic solvents but soluble

in sodium and ammonium hydroxides and concentrated sulfuric acid. Sodium salts of all were prepared.

Analyses of the dyes and their sodium salts.

(XIII) Calcd. for $C_{16}H_{18}O_7N_2SSb$: Sb, 24.4. Found: 22.6.

Calcd. for $C_{16}H_{18}O_7N_2SNa_3Sb$: Sb, 21.3. Found: 20.1.

(XIV) Calcd. for $C_{16}H_{14}O_7N_2Sb$: Sb, 23.7. Found: 22.4

Calcd. for $C_{16}H_{11}O_7N_2Na_3Sb$: Sb, 21.0. Found: 19.4.

(XVI) Calcd. for $C_{16}H_{14}O_7N_2S_2Sb$: Sb, 21.0. Found: 20.3.

Calcd. for $C_{16}H_{10}O_9N_2Na_4Sb$: Sb, 18.2. Found: 19.5.

The preparation of compounds of Series III which could not be precipitated with acid occasioned much difficulty. By concentrating to very small volume and making the solution very strongly acid with hydrochloric acid, small yields could be obtained. Several methods were attempted in order to isolate the dye. A concentrated solution of the dye was treated with a saturated solution of sodium chloride in an effort to salt out the dye. This method was not very satisfactory as the precipitate contained much salt and, in addition, a large amount of the dye remained in solution. Fractional precipitation from alcohol-water mixture gave fair results but the method was very tedious and the yields were poor.

The method finally adopted was the precipitation of the barium salt of the dye by treating the solution with a solution of barium chloride. The barium salts of the dyes separate out as apparently amorphous precipitates. These precipitates are collected by filtering the solution or by centrifuging, washed thoroughly and dried. Fortunately, the barium salts of the intermediates used to make these dyes are relatively soluble in water and if any of them precipitate with the dye, washing with water removes them. The dried compounds were weighed and then suspended in water. To these suspensions a dilute solution containing sufficient sodium sulfate to precipitate the barium was added. In fact, it is better to add a slight excess of sodium sulfate to prevent the presence of the highly toxic barium ion in the final product. The mixtures were warmed and stirred vigorously. Barium sulfate was thrown down and the sodium salts of the dyes went into solution. A small amount of the dyes is adsorbed on the precipitates, coloring them highly. The barium sulfate was filtered off and the resulting solutions of the sodium salts of the various dyes were evaporated to dryness either on a water-bath or "in vacuo." It is better to dry in a vacuum. Each was tested for barium to insure its absence.

Diazotized stibanilic acid was coupled with H-acid, R-salt and chromotrope, respectively, to give compounds XII, brilliant purple; XV, orange brown; and XVII, purple. These are all soluble in water, insoluble in organic solvents and soluble in concentrated sulfuric acid. They decompose on heating.

Analyses:(XII) Calcd. for $C_{10}H_{10}O_{10}N_3S_2Na_4Sb$: Sb, 17.9. Found: 19.5.(XV) Calcd. for $C_{10}H_9O_{10}N_3S_2Na_4Sb$: Sb, 18.2. Found: 17.2.(XVII) Calcd. for $C_{16}H_{10}O_{11}N_3S_2Na_4Sb$: Sb, 17.8. Found: 16.9.

For comparison, the analogs of all of these dyes were prepared from diazotized sulfanilic acid and the same intermediates. These were isolated as the sodium salts. They have been utilized as dyes for the dyeing of woolen skeins and have also been tested pharmacologically on rats infected with *Trypanosoma equiperdum*.

Miscellaneous

Several antimony compounds which do not belong to any of these classes of dyes have been prepared. The general method of preparing these derivatives has been the application of the diazo reaction for introducing the stibinic acid group. As a consequence, various aromatic amines have been the starting-point for all of the subsequent syntheses.

May found that a double salt of diazotized sulfanilic acid and antimony trichloride could not be prepared, due in all probability to the strong acidic character of the sulfonic acid group. This has been confirmed and also has been found to apply to diazotized anthranilic acid. That the formation of the double salt is prevented by the presence of the acidic groups seems to be indicated strongly by the fact that we have been able to prepare antimony trichloride molecular double salts with diazotized methyl anthranilate and with *p*-aminobenzoic acid. The latter compound is formed with some difficulty. These double salts have been broken down with sodium hydroxide to form the corresponding stibinic acid derivatives.

Antimony compounds have also been prepared from diazotized benzidine, *p*-aminodimethylaniline and *p*-aminodiethylaniline.

The method of preparation has been the same in every case. Tenth molar proportions of the amine and antimony trioxide were dissolved in 100 cc. of water and 60

TABLE I
ANTIMONY COMPOUNDS

Molecular compound	Stibinic acid	Analysis, % Sb, Calcd. Found
$(CH_3)_2NC_6H_4N_2Cl.SbCl_3$ —white crystals ^a	$(CH_3)_2NC_6H_4SbO_3H_3$ —white	41.7 40.8
$(C_2H_5)_2NC_6H_4N_2Cl.SbCl_3$ —greenish crystals ^a	$(C_2H_5)_2NC_6H_4SbO_3H_3$ —white	38.0 36.1
$C_6H_4N_2Cl.SbCl_3$ $C_6H_4N_2Cl.SbCl_3$ —light yellow crystals	$C_6H_4SbO_3H_3$ —yellow	49.1 54.0
$C_6H_4 \begin{cases} COOCH_3 \\ N_2Cl.SbCl_3 \end{cases}$ —white crystals	$C_6H_4 \begin{cases} COOCH_3 \\ SbO_3H_2 \end{cases}$ —white	39.3 42.1

^a These crystals were contaminated with the *p*-nitroso-di-alkyl aniline, which gave them a greenish tinge.

cc. of concentrated hydrochloric acid. This solution was cooled to 0° and a 10% water solution of 6.9 g. of sodium nitrite was added through a capillary at the bottom of the beaker, the contents being stirred rapidly. The crystalline double salts, being comparatively insoluble in hydrochloric acid of this concentration, settled out. These were filtered off and suspended in water and this suspension was added slowly to 10% sodium hydroxide at 90°. During the addition the mixture was stirred mechanically and a brisk evolution of nitrogen took place. After this reaction was over, the by-products were precipitated by making the solution almost neutral and passing in carbon dioxide. The sodium salts of the various aromatic stibinic acids were then precipitated by adding alcohol. These salts were obtained by filtering and were dissolved in water and the acid form of the compounds precipitated by dilute acetic acid.

These products were insoluble in water and the usual organic solvents but soluble in sodium and ammonium hydroxides. They decomposed on heating (see Table I).

Analytical

The analyses of these compounds occasioned some difficulty and many methods were tried. The method of Schmidt with a slight modification was used with fair success. After the sample had been burned down with 5 g. of sodium bisulfate and 10 cc. of concentrated sulfuric acid and diluted tartaric acid was added, sulfur dioxide was passed through to insure the reduction of all pentavalent antimony. The excess sulfur dioxide was removed by boiling, preferably in an atmosphere of carbon dioxide. The solution after cooling was neutralized with sodium bicarbonate and then titrated with 0.1 *N* iodine solution.

The method of Macallum works satisfactorily for the water-soluble compounds.

The use of the Parr bomb for oxidation of the sample with sodium peroxide was attempted. The subsequent procedure was: acidification with hydrochloric acid, filtering, adding cooled solution to a solution of 5 g. of potassium iodide in 100 cc. of water and titrating liberated iodine with 0.1 *N* thiosulfate. The results, using this method, were low.^{7,8,9,10}

Pharmacological

All the derivatives of these three series of antimony dyes have been tested against a virulent strain of *Trypanosoma equiperdum*. The white albino rat has been used as a test animal. One per cent. solutions of the dyes were utilized and the results are summarized in Table II.

A more complete report on the pharmacology of these compounds will appear elsewhere.

Antimony and the Color of Dyes

In view of the fact that the compounds described are dyes, it was thought of interest to ascertain the effect of the antimony group as an auxochrome.

⁷ Rohmer, *Ber.*, **34**, 1565 (1901).

⁸ Fargher and Gray, *J. Pharmacol.*, **18**, 356 (1921).

⁹ Macallum, *J. Soc. Chem. Ind.*, **42**, 468T (1923).

¹⁰ Schmidt, *Ann.*, **421**, 244 (1920).

TABLE II
 GENERAL SUMMARY

Compound	Sb content	Toxic dose, g. per kg.	Effective dose	Chemotherapeutic index	Attempts	Cures	Remarks
I to VIII	3 each	0	Practically non-toxic. All compounds of these series useless.
XII	19.5	0.3	0.05	6-7	14	8	
XIII	20.1	.3	.1	...	5	0	Effective for mild infection.
XIV	19.4	.4	.09	4-5	8	3	Cures with treatment give promise.
XV	17.3	.4	.1	...	5	0	Effective with mild infection.
XVI	17.5	.4	.08	4-5	10	6	
XVII	16.9	.4	5	0	Effective with mild infection.

Accordingly, dyes were made for this purpose by coupling diazotized stibanilic acid with various intermediates, and for comparison diazotized sulfanilic acid was coupled with the same intermediates. The intermediates used for this purpose were as follows: H-acid, Neville and Winther's acid, J-acid, R-salt, G-salt, Armstrong's acid, Epsilon acid, Schaeffer's salt, chromotrope, phenol, chlorophenol, *o*-cresol, *o*-nitrophenol and salicylic acid.

Woolen and cotton skeins, five grams in weight, were utilized for application of the dyes. Solutions of each dye were prepared in such a manner as to give a 1% dyeing, based on the weight of the skein. Calculated quantities of solutions containing known amounts of diazotized stibanilic and sulfanilic acids, respectively, were pipetted into beakers containing dilute solutions of the requisite amounts of the various intermediates, these solutions being alkaline with sodium carbonate. The technique of the ensuing manipulations is that described by Waldron and Reid¹¹ for the dyeing of woolen and cotton skeins, respectively.

It was found that the antimony dyes had the property of being direct

 TABLE III
 COLOR OF DYES

Intermediate	Auxochrome groups		
	—SO ₂ H (wool)	—SbO ₂ II ₂ (wool)	—SbO ₂ II ₂ (cotton)
H-acid	Bordeaux *	Reddish violet	Light violet
Neville and Winther's acid	Bright reddish orange	Light red	Dull pink
R-salt	Light dull reddish orange	Dull yellowish red	Pale dull reddish orange
G-salt	Very light buff	Pale dull yellowish orange	Very pale, dull reddish orange
Epsilon acid	Bright yellowish brown	Bright yellowish brown	Dull reddish orange
Chromotrope	Cerise	Dull reddish violet	Light bluish violet
Schaeffer's salt	Dull reddish yellow	Orange	Very dull reddish orange
Chlorophenol	Dull yellow	Light dull yellow	Dull cream
Cresol	Greenish yellow	Dull yellow	Cream

¹¹ Waldron and Reid, *THIS JOURNAL*, **45**, 2412 (1923).

dyes for cotton, whereas the sulfanilic acid derivatives were not fast to cotton and were completely washed out.

The colors of the resulting skeins indicate that the antimony group (the stibinic acid group) is more strongly auxochromic in character than is the sulfonic acid group. Table III lists the colors of the various dyes.

Our thanks are extended to Dr. R. E. Rose, of the Technical Laboratory of E. I. du Pont de Nemours and Co., who kindly furnished the skeins for this work and the color designations of the finished products, and also to Mr. C. Slagle of this Laboratory who assisted in preparing the dyed skeins.

Summary

1. The method of preparing stibanilic acid has been improved.
2. Three series of azo dyes containing antimony have been made and tested against trypanosomiasis in the white rat.
3. The effect of antimony on color has been ascertained.
4. Several other antimonials have been described.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

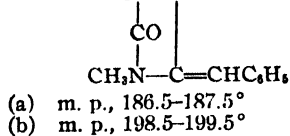
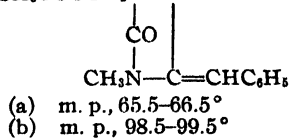
VARIOUS EFFECTS PRODUCED BY THE ACTION OF LIGHT UPON THE ISOMERIC MODIFICATIONS OF CERTAIN POLYPEPTIDE-HYDANTOINS

BY DOROTHY A. HAHN AND JANET EVANS

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As a result of the investigation of a fairly large number of pairs of geometrical isomers corresponding to different derivatives of benzal¹ and anisalhydantoin,² the interesting observation has frequently been made that during the process of preparation and purification of these substances, minute quantities of very high-melting and very insoluble compounds were formed. These substances were markedly different in their properties from any of the major products taking part in the particular transformations but were never formed in quantities sufficient to admit of a study of their properties or even of their analysis. Recent work on the isomeric modifications of methyl-N-3-methylbenzalhydantoin-N-1-acetate and of the corresponding acids,¹ has at last made it possible to arrive



¹ Hahn and Evans: The preparation and properties of these substances have been described in a paper which was received by THIS JOURNAL, July 23, 1927.

² Hahn and Gilman, THIS JOURNAL, 47, 2953 (1925).

at a definite and more or less detailed knowledge of some of the conditions which favor the formation of these very insoluble and high-melting compounds. The phenomenon has, for example, now been shown definitely to involve either a polymerization or an intramolecular rearrangement of a single pure substance and to be accelerated if not induced by the action of light. The changes which take place occur slowly in the presence of ordinary daylight, are hastened by bright sunlight and are very markedly accelerated under the influence of ultraviolet light from a mercury arc lamp. Certain of these compounds have been observed to suffer these changes when exposed to light in the *solid* state but the transformation is distinctly favored by the solution of the substance either in alcohol or ether. In particular, ether solutions which contain minute traces of iodine as a catalyst have been observed to give very satisfactory results under the action of ultraviolet light. The rate of transformation varies to a marked degree under what appear to be the same conditions in the case of different substances. The changes which are produced by the action of light are not limited to the formation of the above-mentioned high-melting and insoluble compounds but are fairly complex, as will be apparent from a consideration of the following examples.

I (a) The lower-melting ester, m. p., 65.5–66.5°, whether present in solid crystalline form or when partially dissolved and partially suspended in alcohol or ether, is transformed under the action of light in the following three ways: (i). It isomerizes to give the corresponding higher-melting modification. This was identified by a mixed melting-point determination with an analyzed specimen, m. p., 98.5–99.5°, which had been obtained by synthesis.³ (ii) It decomposes with the splitting off of benzaldehyde. This product was identified by its odor, its reaction with Tollens' reagent and finally by its conversion into benzoic acid. The benzoic acid which was produced in this way was identified by its properties and by a mixed melting-point determination with a pure laboratory specimen (Kahlbaum preparation). This decomposition takes place spontaneously even when pure, dry crystals are allowed to stand in stoppered glass containers, so that the substance cannot be kept unchanged under any conditions prevailing in the laboratory for periods of more than a few months. Incompletely purified specimens, m. p., 63–66°, begin to show signs of decomposition in the course of one week. The other product or products resulting from this decomposition have not been isolated. (iii) It polymerizes or isomerizes to form a substance which is very insoluble in all ordinary solvents and which melts at 278°.

I (b). The corresponding higher-melting ester, m. p., 98.5–99.5°, behaves in much the same way as the lower-melting ester under the action

³ The same change is produced very rapidly and quantitatively in alcohol solution under the action of hydrogen chloride gas. Compare Ref. 1.

of light but is distinguished by the fact that it is relatively much more stable and that its rate of transformation is relatively slower.

(i) It isomerizes to give the corresponding lower-melting modification, m. p., $65.5-66.5^{\circ}$, which was identified by comparison with the analyzed specimen. (ii) It decomposes with the formation of benzaldehyde, which latter was identified as described above. (iii) It polymerizes or isomerizes to give the same insoluble product, m. p., 278° , that was obtained in the case of the lower-melting isomer. The identity of the product which was obtained in the two cases was established by analyses and by means of a mixed melting-point determination.

II (a). The lower-melting corresponding acid, m. p., $186.5-187.5^{\circ}$, appears to be extremely stable under the action of light and suffered no appreciable change in its melting point on standing and no precipitation of an insoluble compound from its solutions even after these had been exposed to radiation from a mercury arc lamp over a period of many weeks.⁴

II (b). The higher-melting isomer suffers the following transformations under the action of light:

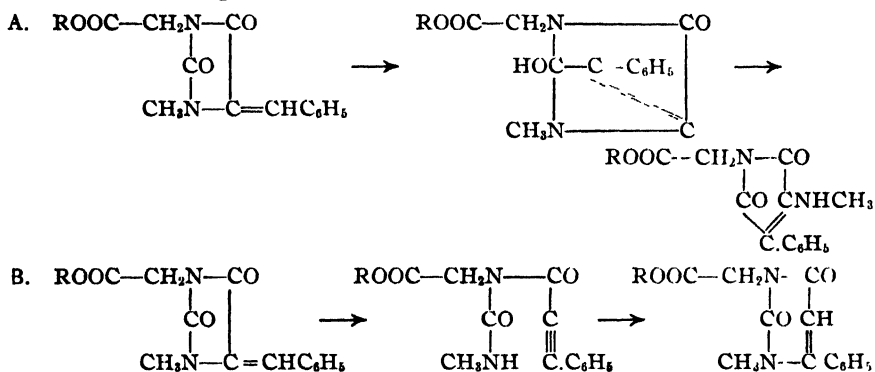
(i) It isomerizes to give the lower-melting modification, which was identified by means of a mixed melting-point determination with a pure analyzed specimen. (ii) It has not been observed to decompose with the splitting off of benzaldehyde. (iii) It polymerizes or isomerizes to give an acid which melts with decomposition at $290-294^{\circ}$. This substance is extremely insoluble in all ordinary solvents, but may be recrystallized from boiling acetic acid. It is not identical with the insoluble product which was obtained from the corresponding esters, since a mixture of the two products melted at $265-288^{\circ}$. The product from the esters is neutral to litmus and phenolphthalein, while the product from the above acid shows distinctly acid properties.

A comparison of these results shows that two different insoluble and high-melting rearrangement products are formed by the action of light upon the isomeric modifications of methyl-N-3-methylbenzalhydantoin-N-1-acetate (I, a and b) and upon the corresponding higher-melting acid (II, b), respectively. This is significant in that it suggests at once that the $-\text{COOCH}_3$ and $-\text{COOH}$ groups are still intact in the final product of the reaction. A comparison of the results which were obtained from the analysis of the two products, moreover, approximates very closely to the results obtained from the analysis of the original ester and acid, respectively. Further, the insoluble acid product, m. p., $290-294^{\circ}$, exactly neutralizes one equivalent of base, the reaction being accompanied by the

⁴ It is, however, rapidly and quantitatively transformed into the corresponding higher melting isomer when its acetic acid solution is boiled with hydrochloric acid. Compare Ref. 1.

complete solution of the substance. These facts admit of the assumption that the transformation has been of the nature either of a polymerization (which could be accounted for by the presence of unsaturated ethylene linkages in the original esters and acid) or of an isomerization reaction. The possibility that the reaction is one of polymerization cannot, unfortunately, be settled by means of molecular weight determinations, since the products under consideration are too insoluble to admit of laboratory manipulation by either boiling- or freezing-point methods.

In the event of isomerization two possible rearrangements might be conceived to take place:⁵



The corresponding acid might in either case be assumed to behave similarly. If a compound of the first type were formed, it should show basic properties as it contains a CH_2NH group. Since, however, neither of the high-melting products is soluble to any extent in concentrated hydrochloric acid, the possibility of a rearrangement of this kind would seem to be discounted. On the other hand, the rearrangement of the hydantoin to a pyrimidine would, according to advices from Dr. Johnson, be in general agreement with the observed solubilities of the new products, and if, by any chance, such a transformation can actually be demonstrated it would represent a new generic relationship between hydantoins and pyrimidines and would be of immediate biochemical interest. Typical illustrations of the procedures which have been employed will now be given.

Experimental

The tendency of methyl-N-3-methyl-4-benzalhydantoin to undergo decomposition under the action of light was first noticed when a pure, dry, crystalline specimen, m. p., $65.5\text{--}66.5^\circ$, which had been analyzed and left in a stoppered glass specimen bottle was found after the lapse of three

⁵ These two possible configurations have been suggested by Professor Treat B. Johnson and it now seems probable that the synthesis of a pyrimidine corresponding to the second formula (B) will be attempted next year by Miss Evans at Yale University under the direction of Dr. Johnson.

months to have passed into an oil. When the stopper of the container was removed a strong odor of benzaldehyde was detected. Other specimens were later observed to behave in the same way, the period of time required for liquefaction varying from two weeks to six months under different conditions. Specimens which were less pure, m. p., 63–66°, liquefied very rapidly. The process was also found to be accelerated by radiations from a quartz mercury arc lamp.⁶ The oily products which were obtained in a series of experiments were combined and distilled with steam. The steam distillate yielded a small amount of solid material which was removed by filtration. It melted at 115–118° and after recrystallization from water was identified as benzoic acid by means of a mixed melting point with a pure specimen of benzoic acid of known constitution. Samples of the aqueous filtrate from this substance when treated with 'Tollens' reagent gave a silver mirror. The main portion of the distillate was, therefore, oxidized with permanganate, neutralized with sodium hydroxide and evaporated to small volume. The clear solution which was obtained in this way, when acidified with hydrochloric acid, gave a precipitate of benzoic acid which was identified by comparison with a pure specimen of this substance. An oily residue which remained in the distilling flask after the steam distillation was separated from the supernatant aqueous layer and treated with alcohol. This procedure resulted in its partial solution and the simultaneous separation of an insoluble substance which melted at 276–278°. The alcohol filtrate from the latter was found to contain a mixture of the two isomeric esters II and III. These were partially separated by a process of fractional crystallization.

When the ester, m. p., 65.5–66.5°, was dissolved in alcohol or ether and the clear solution allowed to stand in diffused daylight, it gradually became cloudy and a fine, white, crystalline precipitate was observed to settle on the bottom and walls of the containing vessel. The formation of this precipitate was greatly accelerated by subjecting the solution to the radiations from a mercury lamp. Under this treatment, continued over a period of two weeks in the presence of a trace of iodine as a catalyst, 1.0 g. of ester, m. p., 65.5–66.5°, yielded approximately 0.1 g. of insoluble precipitate, m. p., 276–278°. The alcohol filtrate from this substance smelled strongly of benzaldehyde and on evaporation yielded 0.4 g. of a substance melting at 94–98°. This after recrystallization from alcohol was identified as the higher-melting, isomeric modification of the original ester by comparison with a pure specimen of known constitution. The alcohol filtrates from this substance when combined and evaporated yielded an oil which did not crystallize.

The ester (III), m. p., 98.5–99.5°, was observed to behave similarly. Thus, pure crystalline analyzed specimens which had stood in glass-stoppered containers for a period of one year were found to have become opaque and to have suffered a change in melting point to 97–245°. When recrystallized from boiling alcohol, this mixture was readily

⁶ 220-volt, direct current type, manufactured by the Hanovia Chemical and Manufacturing Company, Newark, N. J.

resolved into an insoluble substance, m. p., 276–278°, which was removed by filtration, and the original ester, m. p., 94–98°. The same effect was produced in ten weeks by exposing a sample of the ester to the action of radiations from a mercury lamp. In this case the product melted at 90–235°, while a sample of the same specimen which was kept in the dark showed no appreciable change in its melting point. The formation of the insoluble substance, m. p., 276–278°, was still further accelerated by partly dissolving and partly suspending the ester, m. p., 98.5–99.5°, in alcohol or ether and subjecting the mixture to the action of radiations from a mercury lamp. Thus 5 g. of ester suspended in 80 cc. of alcohol-free ether and exposed in this way for three weeks yielded 0.2 g. of an insoluble substance melting at 274–278°. In this case 3.6 g. of the original ester, m. p., 94–98°, was recovered and in addition to this 0.2 g. of the lower-melting isomer, m. p., 65.5–66.5°, was isolated as the result of fractional recrystallization of the resulting mixture from alcohol. Traces of benzoic acid were also separated and identified. The formation of the insoluble substances, m. p., 274–278°, appears to represent a time reaction. Thus, in general a clear ether solution becomes cloudy in the course of about a week and in two weeks an appreciable precipitate has formed. If this is removed by filtration and the clear filtrate exposed to the further action of light an *immediate* cloudiness becomes apparent. It should be noted that invariably at the beginning of any experiment there appears to be an appreciable period of time (usually about one week) which is required for the initial reaction. In one case 1.7 g. of ester, m. p., 98.5–99.5°, dissolved in 80 cc. of cold methyl alcohol became slightly turbid after a lapse of 15 hours and yielded 0.2 g. of a precipitate, m. p., 274–277°, after an exposure of three weeks.

The insoluble products, m. p., 274–278°, which were obtained as the result of these experiments were found to be identical whether formed from the lower- or higher-melting esters. This material as obtained from all sources was combined and purified by recrystallization from boiling benzene. The process was an extremely tedious one because of the very slight solubility of the substance (0.3 g. in 600 cc.) but was satisfactory in so far that a pure product melting sharply at 278° was finally obtained.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.21. Found: 10.26.

This composition is the same as that found in the case of the original esters⁷ m. p., 65.5–66.5° and 98.5–99.5°, respectively.

The corresponding isomeric acids, m. p., 186.5–187.5° and 198.5–199.5°, respectively, were observed to differ from each other very considerably in their behavior under the action of light. The former appears to be remarkably stable both in the solid state and in solution. Some action takes place as shown by a change in melting point to 150–180° after an exposure of five months. The change was, however, not sufficient to allow of the separation and identification of any of the transformation products and no trace of an insoluble residue was detected in recrystallizing the above mixture.

The higher-melting isomeric acid, m. p., 198.5–199.5°, was readily transformed into a mixture having a melting point of 190–285° under the action of light. This very definite change was observed in the case of pure, dry, crystalline specimens which had been allowed to stand in stoppered glass containers in ordinary daylight for about a year, but a sample of the same specimen showed an appreciable though smaller change in melting point (to 197–200°) during the course of a month. Both products when treated with alcohol were only partially dissolved and when the resulting solution was filtered an insoluble residue melting with decomposition at 292–294° was obtained.

When the acid, m. p., 198.5–199.5°, partially dissolved and partially suspended in either methyl alcohol or ether, was placed in a quartz bottle and subjected to the action

⁷ Compare Ref. 1.

of radiations from a mercury lamp, the same transformation took place much more rapidly. Thus 5.0 g. of acid gave a precipitate of 0.05 g. of insoluble material, m. p. 292–294°, during the course of two days and the amount of this product increased to 0.3 g. at the end of six weeks. The filtrate from this, on evaporation, yielded 2 g. of a substance which melted at 186–188.5° and which was identified as the corresponding lower-melting isomer after recrystallization and comparison with an analyzed specimen of this compound which had been obtained by synthetic methods. No benzaldehyde was detected as a by-product in any of these transformations. The initial reaction required approximately the same time as was observed in the case of the corresponding esters.

The product melting at 292–294° was not identical with the high-melting and insoluble product which was obtained from the corresponding esters since a mixture of the two substances was found to melt at 265–288°. This new compound is, moreover, an acid which is slightly soluble in water and quickly decolorizes aqueous alkaline solutions containing phenolphthalein. It was, moreover, obtained by boiling 0.1 g. of the product, m. p., 278°, with a mixture of 5 cc. of glacial acetic acid and 10 cc. of concentrated hydrochloric acid for twenty-four hours. The substance is almost insoluble in alcohol, ether and chloroform and so very slightly soluble in benzene that it was not practicable to recrystallize it from this solvent. In this respect it differs markedly from the product, m. p., 278°, which was obtained by the action of light on the corresponding isomeric esters. It is somewhat more soluble in boiling glacial acetic acid (0.5 g. in 1000 cc.), from which it separates in the form of a white, crystalline powder, but unfortunately its melting point was not noticeably improved as a result of this treatment.

Anal. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.77. Found: 9.97, 10.17.

These results correspond closely with those which were obtained in the case of the original acid, m. p., 198.5–199.5°, namely, 10.65 and 10.63. The fact that the values found are so much lower than the calculated might be accounted for by assuming that traces of an impurity are present which could not be removed by recrystallization from acetic acid.

This new acid exactly neutralizes one equivalent of potassium hydroxide as calculated for its simplest molecular formula. Thus, when 0.0346 g. is suspended in 40 cc. of water, to which a drop of phenolphthalein has been added, and titrated against standard potassium hydroxide, it passes into solution and an end-point is reached when 0.0086 g. of base or an equivalent of 0.0059 g. of potassium has been added. The calculated amount of potassium required to neutralize an acid having the formula $C_{13}H_{12}O_4N_2$ is equal to 0.0052 g.

Summary

Certain types of hydantoin derivatives which contain unsaturated ethylene linkages and which exist in geometrically isomeric modifications undergo three distinctly different types of rearrangement and decomposition when subjected to the action of light. While the exact nature of these changes is not known in all cases, the phenomena would seem to be of definite importance from the standpoint of biochemistry.

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[CONTRIBUTION FROM THE DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND
AGRICULTURAL BACTERIOLOGY, UNIVERSITY OF WISCONSIN]

THE OCCURRENCE OF CALCIUM CITRATE CRYSTALS IN CULTURES OF BUTYRIC ACID-FORMING BACTERIA AND THE WATER OF CRYSTALLIZATION OF CALCIUM CITRATE

BY W. H. PETERSON, P. W. WILSON,¹ ELIZABETH MCCOY¹ AND E. B. FRED

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When milk or potato to which calcium carbonate has been added is fermented by certain strains of butyric acid bacteria, white granules varying in size from 0.1 to 1 mm. in diameter appear in the medium. These granules have been analyzed and found to be calcium citrate. Somewhat similar crystals have been reported by Sato² to occur in sweetened condensed milk. The granules are formed by both groups of anaerobic butyric acid bacteria; those that form butyl alcohol (*e. g.*, *Clostridium acetobutylicum*, Weizmann) and those that do not (*e. g.*, *B. saccharobutyricus*, von Klecki).

Experimental

Preliminary Examination.—The granules were removed by diluting the medium with water and picking out the particles with a pair of forceps. Under the microscope they appeared to be snow-white, crystalline balls from which little, blunt, prism-like needles projected in all directions. The crystals were practically insoluble in water but could be dissolved by acidifying slightly with hydrochloric acid and boiling. A small quantity of organic debris remained undissolved. The crystals gave strong positive tests for citric acid with Denigès',³ Kunz's³ and Naüssler's⁴ reagents.

Analysis of the Crude Crystals.—The crystals were dried at 110° and analyzed, with the following results: ash, 23.0%; calcium, 17.5–18.2%; phosphorus, 0.11%. A small percentage (1.90) of the ash was insoluble in hydrochloric acid diluted with an equal volume of water.

Purification and Analysis of the Salt.—The crude salt was dissolved in dilute hydrochloric acid, the solution was filtered, neutralized with calcium hydroxide and calcium citrate precipitated by heating to boiling. The precipitate was filtered off and dried to constant weight in a desiccator and then dehydrated by heating at 110° for forty-eight hours.

Anal. Subs., 0.1348: loss (110°) 0.0164. Calcd. for $\text{Ca}_2(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$: H_2O , 12.63. Found: 12.17.

The calcium in the anhydrous salt was as follows.

¹ Research Fellow of the Commercial Solvents Corporation, Terre Haute, Indiana.

² Sato, U. S. Dept. Agr. Dairy Div., World's Dairy Cong. Proc., II, 1285, 1923.

³ Abderhalden, "Handbuch der biologischen Arbeitsmethoden," Urban und Schwarzenburg, Berlin, 1925, abt. I, teil 6, pp. 720, 722.

⁴ Naüssler, *Chem.-Ztg.*, **38**, 937 (1914).

Anal. (ignition). Subs., 0.0538, 0.1050: CaO, 0.0182, 0.0355. *Calcd. for* $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$: Ca, 24.13. Found: 24.16, 24.19.

Origin of Citric Acid.—In order to determine if the citric acid in this compound was that occurring naturally in the media or was formed by the organism in the fermentation of the sugar, a number of milk cultures were fermented. All of the flasks contained granules but the number and size varied. The granules were dissolved by adding glacial acetic acid and boiling. An equal quantity of acid was added to the control flasks. After making up to their original volume, the citric acid in the control and fermented samples was determined by Denigès's method. As a check on the method, known quantities of citric acid were added to certain aliquots before analysis. Complete recovery of the added citric acid was obtained. The unfermented milk contained 0.21% of citric acid and the fermented milk from 0.04 to 0.17%. Cultures that showed a small number of granules were low in citric acid, while cultures that contained a large number of granules were correspondingly high.

These results indicate that the bacteria as such are not directly concerned with the formation of the crystals but bring about changes in the composition of the milk that favor the formation of the crystals from the calcium and citric acid normally present. The action of the bacteria was duplicated by acidifying the milk with an amount of acetic and butyric acids equivalent to that formed by the bacteria (100 cc. of 0.1 *N* per 100 cc. of milk). Better results were obtained by first digesting the milk with trypsin and then acidifying. Under these conditions the crystals were larger and more numerous than in the fermented milk. In the untreated milk, crystals eventually appeared but these were small in comparison to those formed in the treated samples. The size and rate of formation of the crystals appear to be dependent on the colloidal properties and hydrogen-ion concentration of the milk.

Water of Crystallization of Calcium Citrate.—In discussing the composition of the granules, it was stated that the calcium citrate was completely dehydrated at 110° and that at this temperature the theoretical water of crystallization and percentage of calcium were obtained. These results are not in agreement with the statements in Abderhalden,⁶ Meyer and Jacobson,⁷ Beilstein⁸ and other reference works which say that calcium citrate, $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$, loses 2 molecules of water between

⁶ Barthel, "Methods Used in the Examination of Milk and Dairy Products," translated by Goodwin, Macmillan and Co., London, 1910, p. 91.

⁷ Abderhalden, "Biochemische Handlexikon," Julius Springer, Berlin, 1911, I, p. 1179.

⁸ Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit and Co., Leipzig, 1913, 2nd ed., I, Teil 2, p. 714.

⁸ Beilstein, "Handbuch der Organische Chemie," Julius Springer, Berlin, 1921, 4th ed., III, p. 564.

110–130° and the other 2 molecules only when heated to 175–185°. These statements are apparently based on the work of Soldaini and Bertè.⁹ Perhaps Soldaini and Bertè were led to use these high temperatures because the earlier workers, Heldt¹⁰ and Kämmerer¹¹ had dried their salts at 200° and 210°, respectively. In a recent publication Chatterjee¹² concluded on the basis of the calcium content that the citrate when dried at 110° retained but one-half a molecule of water. As we had obtained close to the calculated values for 4 molecules of water of crystallization and calcium for the dehydrated compound by drying at 110°, it seemed necessary, therefore, to redetermine the loss of water of calcium citrate under varying conditions of pressure and temperature.

Calcium citrate was first prepared by neutralizing citric acid, using phenolphthalein, with lime water, filtering and boiling for a few minutes to precipitate the calcium citrate. After standing on the steam-bath for two to three hours, the precipitate was filtered off, washed with water, alcohol, and ether, and dried in the air for twenty-four hours. A second preparation was made by neutralizing the citric acid with sodium hydroxide, adding calcium chloride and boiling. The precipitate which formed was treated in the same manner as in the first method. This preparation was somewhat coarser than the first preparation and, as the table shows, contained less hygroscopic moisture. In all, seven preparations were made by the two methods. The loss of the water of crystallization under various conditions of temperature and pressure was determined. As a check on the results the dried samples were also analyzed for calcium. The samples were kept between watch glasses with tightly-fitting, ground-glass edges held in place by a spring clamp. The watch glasses could thus be opened during the drying and closed during the weighing. After each drying samples were taken for calcium analysis and the remainder again dried to constant weight before calculating how much sample had been taken. This procedure was found to be necessary owing to the great rapidity with which the dried salt took up water on exposure to the air. The calcium citrate was strongly ignited until the weight became constant and this weight was taken as that of the resultant calcium oxide. As a check on the result, the calcium in the calcium oxide was also determined by the permanganate method.

The data for 4 preparations are given in Table I. The amount of hygroscopic water held by the citrate varies with the fineness of division of the powder. The light, fluffy material, Preparation No. 1, contained more than twice as much water as the denser material, Preparation No. 2. A third preparation which was not washed with alcohol and ether but was air-dried for thirty-six hours contained over 12% of hygroscopic moisture.

Contrary to the statement of Soldaini and Bertè, calcium citrate may lose water of crystallization when dried in a vacuum over sulfuric acid. In eighteen hours the two preparations lost 4.36 and 4.88%, respectively. The loss is probably not a constant quantity but varies with the degree of vacuum, the physical state of the citrate and other factors.

⁹ Soldaini and Bertè, *Gazz. chim. ital.*, **29**, 489 (1899).

¹⁰ Heldt, *Ann.*, **47**, 157 (1843).

¹¹ Kämmerer, *Ann.*, **148**, 294 (1868); **170**, 176 (1873).

¹² Chatterjee, *J. Phys. Chem.*, **28**, 1009 (1924).

TABLE I
LOSS OF WATER AND CONTENT OF CALCIUM IN CALCIUM CITRATE UNDER VARIOUS
CONDITIONS OF DRYING

Prep. no.	Method of drying	Time of drying, hours	Wt. of sample, mg.	Loss of wt. ^a mg.	%	Calcium in dry salt, ^b %
Experiment I						
1	Desiccator, 20-25°	29	650	34.5	5.30	21.23
2	Desiccator, 20-25°	29	927	17.0	1.83	21.15
1	Desiccator, vacuum, 20-25°	42	505	22.0	4.36	22.00
2	Desiccator, vacuum, 20-25°	42	605	29.5	4.88	22.22
1	Oven, 110°	18	384	31.0	8.08°	24.30
2	Oven, 110°	18	455	34.0	7.47°	24.24
1 and 2	Oven, 125°	18	474	0.0	0.00	24.20
1 and 2	Oven, 180°	12	369	0.0	0.00	24.34
Experiment II						
3	Air	20.70
4	Air	20.95
3	Desiccator, 20-25°	33	622	12.0	1.93	21.06
4	Desiccator, 20-25°	33	584	11.0	1.88	21.09
3	Oven, 110°	26	468	56.0	12.0	24.25
4	Oven, 110°	26	451	54.7	12.1	24.06
3 and 4	Oven, 125°	25	585	0.0	0.0	24.02
3 and 4	Oven, 180°	10	389	0.0	0.0	24.07

^a Water of crystallization in $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ is 12.63%.

^b Calcium in $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ is 21.08%, and in $\text{Ca}_3(\text{C}_6\text{H}_7\text{O}_7)_2$ is 24.13%.

^c Loss in vacuum and at 110° calculated on desiccator-dried material is 12.1 and 12.0%, respectively.

The entire water of crystallization of these preparations was removed at 110° in eighteen hours. More than 90% of this water of crystallization was driven off during the first six hours of heating. The combined loss by drying in a vacuum over sulfuric acid and by heating at 110° is slightly lower than that required for $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ but the calcium content of the dried citrate is that required for $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ and shows that the two drying treatments produced the anhydrous salt. No further loss in weight or change in the percentage of calcium occurred on drying the salt at 125° and at 180°.

In the second experiment the calcium citrate was made from sodium citrate and calcium chloride in the same manner as Preparation 2 in the first experiment. The percentages of hygroscopic moisture in Preparations 3 and 4 are about the same as that in No. 2. The calcium content of the air-dried samples is a little low for $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ and agrees with the moisture determination in proving that the air-dried samples contained some hygroscopic moisture. After being dried in the desiccator over sulfuric acid the salts were found to contain the percentage of calcium required for $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$. When dried at 110° both preparations lost almost the calculated water of crystallization. That the salts were

completely anhydrous is shown by the figures for calcium: 24.26 and 24.06%. Further drying at 125 and 180° did not show any additional loss of weight nor did the percentage of calcium change. The data on these 4 preparations and those found for 3 others not given in Table I demonstrate that certain preparations of $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ lose all 4 molecules of water at 110°. We do not take the position, however, that all preparations of calcium citrate will become completely anhydrous at 110°. Two other preparations which were digested for a longer period of time after precipitation retained small but varying amounts of water (1.20 and 1.88%) at 110° and lost this at 180°. It is possible that the conditions under which the crystals are formed is a factor in determining the firmness with which the water of crystallization is held. The data, however, indicate clearly that no particular number of molecules of water is retained at either 110 or 125°.

Summary

Crystals of calcium citrate appear in old milk cultures (and on potato slants to which calcium carbonate has been added) after fermentation by butyric acid bacteria. The crystals are formed during evaporation of the culture and originate from the calcium and citric acid of the milk. The bacteria hasten the formation of the crystals by digesting the casein and producing a more suitable hydrogen-ion concentration. The same results can be accomplished by digesting the milk with trypsin and acidifying with acetic and butyric acids.

Statements in the literature that $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ retains 2 molecules of water at 125° are incorrect. Seven preparations of calcium citrate were found to lose all of their water of crystallization at 110°. Two preparations retained from 1 to 2% of water of crystallization at this temperature. Drying in a vacuum over sulfuric acid removed more than 35% of the water of crystallization in two instances.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA
AT LOS ANGELES]

THE REACTION OF CHLORO-ACETIC ACID WITH AMMONIA AND THE PREPARATION OF GLYCINE

BY G. ROSS ROBERTSON

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The classical synthesis of glycine¹ from chloro-acetic acid and ammonia has never given entire satisfaction despite various claims in the literature. Although the cost of materials is low, it is significant that Clarke and Taylor² have rejected the method in favor of a two-stage cyanide process involving some expensive reagents. While the latter method is probably the best one now in ordinary use, it affords only 20 to 27% yield, calculated on the basis of the original starting material.

Clarke and Taylor have made valid objection to the Kraut process on account of the trouble in separating the glycine as the copper salt and displacing the copper by hydrogen sulfide. Equally valid is their criticism that the product is contaminated with ammonia, evidently in some form not readily volatilized. It is known, however, that glycine is too weak to form a stable salt with ammonia and can be recrystallized in the free state from ammonium hydroxide. Ammonium chloride is not necessarily the offending impurity, as we have shown in this Laboratory by the preparation of chlorine-free glycine which was seriously contaminated with ammonia.

In the chloro-acetic process the reaction does not stop with glycine but proceeds³ in part to form iminodiacetic acid, $\text{NH}(\text{CH}_2\text{COOH})_2$ and trimethylene-aminetricarboxylic acid $[\text{N}(\text{CH}_2\text{COOH})_3]$ compounds obscurely named "glycollamic acids" in the literature. For brevity they are designated below as "di-acid" and "tri-acid." These acids bearing carboxyl groups in excess of amine nitrogen are strong enough to make fairly stable ammonium salts and thus may furnish the undesired ammonia contamination in a glycine preparation.

It seems reasonable also that either the di-acid or the tri-acid might make a mixed salt or amide with both glycine and ammonia, thus making the impurity persistent in material of low solubility. Several possibilities of cross combination appear in this way and may well account for the fact that in an actual synthesis of glycine the mother liquor, presumably including salts of the di-acid and tri-acid, is an almost uncrystallizable sirup and probably a complex mixture. The sirup does not necessarily contain either chloro-acetic acid or glycolic acid. It has a high content of organic ammonium salts and some residual glycine. Rough Kjeldahl analyses

¹ Kraut, *Ann.*, **266**, 292 (1891).

² Clarke and Taylor, "Organic Syntheses," John Wiley and Sons, New York, **4**, 31 (1924).

³ (a) Heintz, *Ann.*, **122**, 257 (1862); (b) **145**, 49 (1868).

showed that it contains nitrogen in excess of that accounted for as primary amine and ammonia. Its principal role is that of interfering with the crystallization of glycine and of contaminating the product.

The present investigation was first a study of the course of the chloro-acetic acid-ammonia reaction in the interest of increased production of the desired glycine in the original reacting solution. Secondly, the problem was to eliminate the ammonium chloride and organic by-products, thus isolating the crystalline product without resorting to copper compounds.

The first of these plans was tried with the realization that even a moderate increase in the content of glycine would eliminate a corresponding amount of sirupy by-products, particularly the most undesirable tri-acid. If this could be accomplished, there should be a sharp rise in the practical yield of crystalline glycine and a product of much higher purity.

In the second phase of the work, silver oxide was adopted as a reagent to eliminate the normal by-product of ammonium chloride. It was then an easy matter to isolate glycine as the one crystallizable substance remaining. In view of the cost of the silver oxide, a method is described for the easy recovery of the reagent.

The accompanying graph shows the rate of accumulation of glycine in comparison with that of ammonium chloride when a mixture of chloro-acetic acid and ammonia is made in proportions similar to those described in the literature. The period was three hours, with a final determination five days later when the reaction was complete. Production of chloride ion is obviously equivalent to transformation of chloro-acetic acid, and in an ideal case should equal production of glycine if no subsequent reaction took place.

Chloro-acetic acid, twice fractionally distilled and then once recrystallized from an excess of its own melt, was weighed into 15 molar equivalents of chilled conc. ammonium hydroxide (sp. gr. 0.90). The flask containing the mixture was fitted with a wired-in stopper carrying a stopcock and a thermometer. The outfit was immediately placed in a thermostat at 40°. Automatic shaking prevented temperature rise from the heat of the reaction. At intervals portions of the mixture were withdrawn, immediately diluted ten-fold and placed in an ice-bath.

The diluted solution was analyzed at once by the Volhard method for chloride ion, advantage being taken of the fact that unchanged chloro-acetic acid does not react with silver ion. As time permitted, an aliquot of each reaction sample was rapidly boiled with a moderate excess of sodium hydroxide until ammonia fumes could not be detected for a final ten minutes. The content of primary amine (glycine) was now estimated in each by the standard van Slyke de-amination method. The macro-apparatus was used with the customary corrections. From each numerical result 3%⁴ was deducted, to allow approximately for the abnormal evolution of gas in the de-amination of glycine. Finally, Volhard titrations repeated several hours after the samples went on ice showed no appreciable change.

While ammonia is being expelled from the analytical samples, two slight errors enter. A small amount of new glycine is formed before the ammonia

⁴ Van Slyke, *Ber.*, 44, 1684 (1911).

is gone and a small amount of glycine is eliminated by reaction with the excess chloro-acetic acid before the latter is all transformed by the alkali into sodium glycolate. Since these errors tend to compensate, as sodium hydroxide in boiling dilute solution does not hydrolyze glycine, and since the traces of residual ammonia would not vitiate the de-amination data to a significant extent, it is thought that the nitrogen values are reasonably accurate for the use in question.

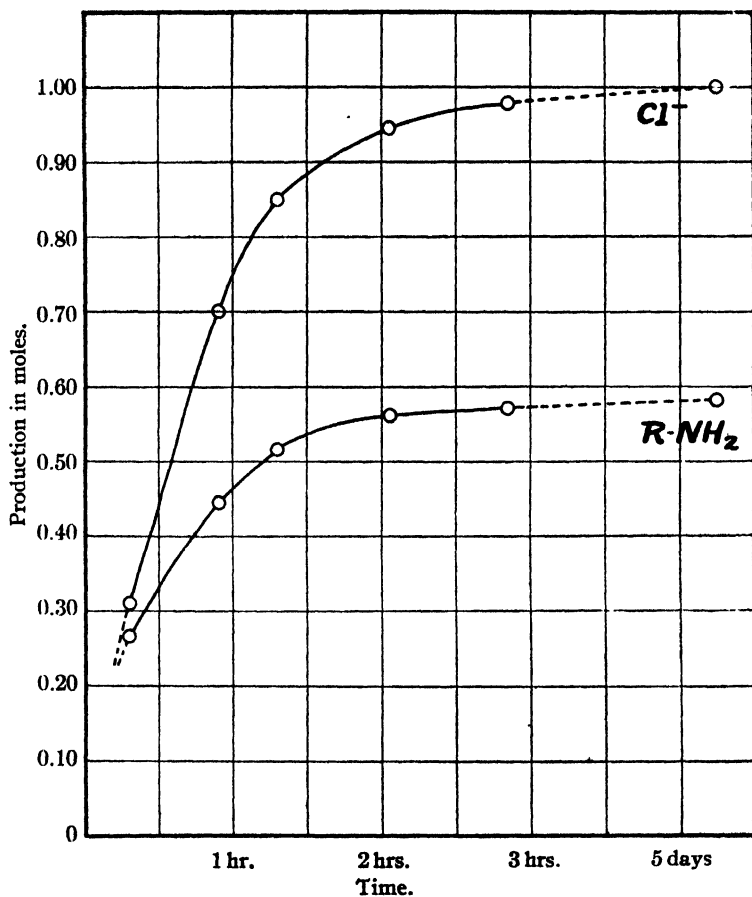


Fig. 1.—Transformation of one mole of chloro-acetic acid into ammonium chloride and glycine.

Apparently glycine and chloride ion are produced at nearly the same rate as long as ammonia is in gross excess over glycine. After about 25% production is attained, the accumulated glycine goes astray so rapidly that nearly two-thirds of the subsequent product is lost before the final exhaustion of the chloro-acetic acid is accomplished.

When the above procedure was continued through the silver oxide process described below, only about 20 to 25% yields of glycine were obtained in a fair degree of purity. This material was still decidedly contaminated with ammonium salts.

The obvious moral of the rate experiment was to multiply the ammonia-chloro-acetic acid ratio by about four, thus making the final ratio of chloride ion to glycine more like that at the time of the first analysis (that is, at the 18-minute reaction period of the graph). When this change was made, the final accumulation of glycine at once rose to 86%, and of this 63% was isolated in crystalline form as described later.

Several mixtures of widely variant proportions were analyzed, after two days' standing, by the de-amination method.

Molar ratio, ammonia to chloro-acetic acid	2:1	4:1	6:1	15:1	24:1	60:1	220:1
Primary amine produced, % of theoretical	29	32	37	58	65	86	95

The 220:1 mixture was carried through the full process, yielding 3.0 g. of glycine, or 75% of theoretical. The amount of ammonium hydroxide required in this case is, however, excessive for practical work. As in other cases, the actual yield always falls 20% or more below the potential yield, probably on account of decomposition as well as loss in crystallization and filtration.

Experiments at high temperatures and runs made with 40% ammonia under pressure gave no promise of significant improvement except that derived from raising the ammonia-acid ratio. Experiments with dilute mixtures, those with alcohol as solvent and those with ammonium carbonate⁵ instead of ammonium hydroxide gave inferior results. With reduced-pressure evaporation of the reaction mixture, there were slightly improved yields but the improvement was not worth the trouble. Finally, the 60:1 ammonia ratio was chosen as the best compromise between two evils, namely, excessive volumes of ammonium hydroxide and excessive production of undesired salts.

Preparation of Glycine.—One mole of chloro-acetic acid (94.5 g.) is dissolved in 4 liters of ammonium hydroxide (sp. gr. 0.90) and set aside in a stoppered vessel for twenty-four hours in surroundings at about 30°, or for two or more days at about 20°, no attention being paid to the heat of the reaction. The mixture is then heated to recover the excess ammonia, which is received in a flask of distilled water cooled in running water.

One mole of silver nitrate (170 g.) is dissolved in about 500 cc. of water and converted into flocculent silver oxide by the addition of a slight excess of clear, technical sodium hydroxide solution. The oxide is washed by decantation, collected on a Büchner filter and washed free of sodium compounds.

The glycine reaction mixture is evaporated to about 500 cc., during which time nearly all free ammonia escapes. The silver oxide is then stirred into the solution until no lumps of unchanged reagent can be detected, all residual solid being in the form of

⁵ Nencki, *Ber.*, 16, 2827 (1883).

silver chloride. This excess silver chloride is at once removed on the Büchner funnel. The filtrate is placed in a wide-mouthed flask equipped with a mechanical stirrer to prevent bumping, and is concentrated by boiling. This operation must not be interrupted while ammonia is still present, lest undesirable silver compounds be formed.

When the volume of the solution is reduced to about 200 cc., the silver-ammonia complex is completely decomposed and the rest of the silver chloride precipitated. More water is added and evaporated should there still be traces of silver in solution. The end-point is reached when a drop of aqueous hydrobromic acid, added to the clear supernatant liquid, no longer gives a localized turbidity. The silver chloride is collected on the funnel, and along with the original mass is placed in a 25% solution of technical sodium hydroxide for recovery later.

The glycine solution (vol., 190 cc.) is treated with 1 to 2 g. of Norit, filtered carefully by suction through retentive paper and treated with an equal volume of 95% ethyl alcohol. Pure-white glycine promptly crystallizes but the mixture is allowed to stand for an hour or more on ice. After filtration, washing with alcohol and drying in a desiccator, 43 g. of crystals are obtained. Another like volume of alcohol precipitates an additional 4 g., not quite so pure. It is isolated in like manner after an hour's cooling. Taken as a whole, the glycine contains nearly 0.1 mole per cent. of ammonium salts, judged by Nessler colorimetry.

The total yield of 47 g. is 63% of theoretical, or 0.63 mole. Primary amine left in the mother liquor in one run was 0.09 mole (by de-amination analysis). Total glycine thus accounted for, 0.72 mole. Total glycine originally estimated in solution, 0.86 mole, loss in manipulation, 0.14 mole.

If an ammonia-free product is desired, the glycine is dissolved in 200 cc. of water and shaken for a few minutes with 10 g. of granular permutite (after Folin). The mixture is filtered and 250 cc. of 95% ethyl alcohol slowly stirred into the filtrate. The precipitated glycine, a voluminous crystalline mass of snow-white appearance, is washed on the Buchner funnel with 95% alcohol and dried in a desiccator; yield, 37.5 g., or 50% of the theoretical for the whole process.

PURITY TESTS.—When heated to 230° (corr.) the final product starts to turn brown; it becomes almost black by 238°. In 0.1 *M* solution it shows no appreciable ammonia by Nessler colorimetry. In *M* solution a barely detectable coloration lies between that shown by 10⁻⁵ *M* ammonium chloride and that of the distilled water blank; chloride test, negative.

When permutite was omitted, but no other change made in the procedure, a *M* solution of the product gave Nessler coloration nearly as great as that of 10⁻⁴ *M* ammonium chloride. All tests were made in alkaline solution with allowance for acidity of the glycine. Observations were made immediately on mixing, as glycine soon reacts with Nessler's reagent to vitiate results.

Recovery of Silver.—The following modification of a well-known method⁶ is convenient here.

The moist silver chloride (1 mole) from the glycine process is suspended in about 400 cc. of boiling 25% sodium hydroxide solution contained in a liter beaker. An excess of corn sugar or glucose sirup is cautiously stirred in at a rate slow enough to avoid a sudden violent reaction causing overflow. After a few minutes of boiling the chloride is transformed entirely into a crumb-like mass of finely divided silver.

⁶ Gmelin-Kraut, "Handbuch anorganischen Chemie," Carl Winter's Universitätsbuchhandlung, Heidelberg, 1914, Band V, Abt. 2, p. 8.

By repeated decantations, rapidly made, and copious washing on the Büchner funnel with hot water, soluble matter is removed. A trace of chloride persists, however, but this need not be eliminated if the product is to be used again in the synthesis of glycine.

The silver, still wet, is treated in a liter Pyrex beaker with a slight excess of concd. nitric acid (sp. gr. 1.42). The silver, being very finely divided, is at once converted into silver nitrate, sufficiently pure for use again with glycine.

If the silver nitrate is desired as a laboratory reagent, the acid solution is simply heated until its temperature reaches about 240° , by which time the excess nitric acid is expelled. There is no trouble from bumping as the nitrate is extremely soluble at high temperatures.

The crude silver nitrate is then dissolved in cold water and diluted to 0.75 *M*, whereupon practically all dissolved silver chloride is precipitated. As would be expected, silver chloride is extremely insoluble in silver nitrate of concentrations below molal, but in nitrate solutions of more than molal concentration a considerable quantity of the halide either dissolves or is peptized.

The colloidal silver chloride, usually not in sufficient quantity to warrant salvage, is removed by filtration with the aid of decolorizing carbon. The resulting filtrate upon further dilution does not show the slightest turbidity and is perfectly serviceable as an ordinary reagent.

It is probably not worth while to attempt to make really pure silver nitrate from this recovered solution. It is possible, of course, to fuse the reduced silver and carry out the slow reaction of the compact ingot material with pure nitric acid and thus obtain a pure product.

Incidentally, the above process is very convenient for working up laboratory residues of silver chloride and thiocyanate. With iodide and bromide the process is also satisfactory, but more time should be taken to insure complete reduction with sugar.

Summary

An experimental study of the velocity and course of the reaction between aqueous chloro-acetic acid and ammonia shows that the product, glycine, goes astray seriously into by-products if its concentration is allowed to rise much over 1 mole per cent. of that of the ammonia present.

A method of preparation of glycine is given in which the ratio of ammonia to chloro-acetic acid is 60:1. Ammonium chloride is eliminated by means of silver oxide and a 50% yield of pure glycine obtained.

A simple method is given for recovery of silver oxide with the aid of glucose.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA]

ESSENTIAL OILS IN DESERT PLANTS

I. PHYSICAL CONSTANTS

BY MAXWELL ADAMS AND RUTH BILLINGHURST

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In the semi-arid regions of western United States there is in most localities a stunted growth of plants referred to in general terms as sage-brush, but in reality composed of many widely differing species. The leaves and twigs of most of these plants when crushed have distinct and characteristic odors which indicate the presence of essential oils. Samples of a number of these plants have been collected and steam distilled for the purpose of detecting the presence of essential oils and determining their physical and chemical properties.

Specimens of these various desert plants collected at random, when steam distilled, usually yield from 0.05 to 0.5 of one per cent. of essential oil. The frequent occurrence of these oils has led one of us,¹ in a paper read before the American Association for the Advancement of Science, to suggest that, due to their diathermous properties, they serve, as experiments indicated, as a protection against rapid temperature changes for the plants and also suppress the rapid evaporation of water.

Tests made upon *Artemisia tridentata* prove that the oil exists only in the leaves and young shoots and that the percentage of oil shows a general increase from early spring until late summer. Leaves and twigs of *Chrysothamnus nauseosus* collected from parts of the same plants each month of the year show that the amount of oil varies from 0.04% during May and June to 0.23% in July, 0.39% in August and 0.83% in September. During the winter, when the leaves have fallen, the twigs contained 0.22%. A sample of *Graveolens nauseosus Mohavensis* grown in the botanical gardens at Berkeley, California,² yielded a smaller percentage of oil than the same variety growing in the more arid districts of Nevada.

The cause of these variations is undetermined; it may be due to the stage of development and maturity of the plants, or the increase of the oil during the driest season of the year may be a method of drought resistance developed by the plant.

Among the native plants of the semi-arid regions of the United States, essential oil has been observed in *Artemisia cana*,³ *Artemisia frigida*, *Artemisia Leudoviciana*, *Artemisia caudata*,⁴ and *Ramona stachyoides*.⁵

¹ Adams, *Am. Perfumer*, 17, 348 (1922).

² Supplied by L. A. Waitzinger.

³ Whittelsey, *A New Occurrence of l-Camphor*, "Otto Wallach's Festschrift," Göttingen, 1909, pp. 668-70.

⁴ Frank Rabak, "On Several New Artemisia Oils," *Pharmaceutical Review*, 24, 324-325 (1906).

⁵ Frank Rabak, "Wild Volatile Oil Plants and Their Economic Importance,"

Volatile oil was found by us in the following plants: 1. *Artemisia tridentata typica*, leaves, flowers, and small twigs collected in various localities near Reno, Nevada, at various seasons of the year yielded when distilled from 0.3 to 0.92% of an oil, the first fraction colorless and the last distinctly green. It turns light yellow upon standing. The odor is that of the green plant, strong and very characteristic, and the taste is persistent and camphor-like. The vapors of the oil are tear-producing.

2. *Gutierrezia sarothrae*⁶ collected in September, 1922, near Wedekin Mine, Washoe County, Nevada. The oil from the entire top of the plant is light yellow in color and has a mild but somewhat unpleasant odor.

3. *Juniperus Utahensis*,⁷ leaves and small twigs collected in October, 1923, from trees growing eight miles north of Reno, Nevada, gave on distillation a mobile, colorless oil.

4. *Salvia lanceolata*,⁷ called "purple sage" because of its clusters of small, purple flowers. Leaves, flowers and small branches collected from the rock bluffs along the west shore of Pyramid Lake, Nevada, in June, 1920, and another sample from near Chloride Cliff on the eastern rim of Death Valley, California, May 14, 1926, yielded a clear, strongly fragrant oil.

5. *Thamnosma* (probably *Texanum*) collected from near the Lahontan Dam in Churchill County, Nevada, April, 1916. The shrub is almost leafless and the small thorny branches cut into short pieces and distilled yielded a colorless, fragrant oil.

6. *Tetrademia glabrata*, "spring rabbit brush,"⁸ collected in May, 1915, among the hills northeast of Reno gave on distillation of the flowers, leaves and small branches an ill-smelling oil which darkens readily and grows viscous when allowed to stand for a few days.

7. *Chrysothamnus graveolens*,⁹ tops of plants in flower collected in September, 1915, near the Station Farm, Reno, Nevada, yielded on distillation a colorless oil which soon changed to a light yellow color and when purified consists chiefly of dipentene. The yield varies from 0.04 to 0.85%, depending on the season of the year in which the plants are gathered.

8. *Chrysothamnus viscidiflorens elegans*⁸ collected on the flanks of Slide Mountain, near Franktown, Nevada, October, 1924. The tops when distilled yielded a colorless, ill-smelling oil.

9. *Chrysothamnus nauseosus graphalodes*¹⁰ yielded a light yellow, ill-smelling oil.

Bulletin No. 235, Bureau of Plant Industry, United States Department of Agriculture.

⁶ Identified by L. A. Waitzinger of the U. S. Bureau of Plant Industry.

⁷ Identified by P. A. Lehenbauer of the University of Nevada.

⁸ Identified by N. F. Peterson, Botanist, Nevada Agricultural Experiment Station.

⁹ Identified by S. B. Doten, Director, Nevada Agricultural Experiment Station.

¹⁰ Collected February, 1924, by L. A. Waitzinger at Benton, California, near the Nevada-California state line.

10. *Chrysothamnus nauseosus viridulens*.¹⁰ The smooth, green stems when distilled yielded a yellow oil which became viscous on standing.

11. *Chrysothamnus nauseosus hololeucus*.¹⁰ The white stems of this plant yielded a dark yellow, pleasant-smelling oil.

12. *Chrysothamnus nauseosus Mohavensis*, collected from the botanical gardens at Berkeley, California, March, 1924, yielded a clear, colorless oil with a disagreeable odor.

The distillations were carried out by placing the samples in a wire basket which fitted closely into a tin-lined copper still and passing in steam under a pressure of ten pounds. The distillation was continued for three to four hours. The light oil which floated on the surface was drawn off and purified in each case by a second steam distillation. No attempt was made to extract the oil which remained dissolved in the condensed water. In all cases, therefore, the per cent. of oil present in the specimen is somewhat greater than that recovered. When freshly distilled and dried in contact with potassium carbonate the various oils have the following physical constants.

TABLE I
PHYSICAL CONSTANTS OF THE OILS

Name	Essential oil in plant, %	Sp. g. (18°)	B. p., °C. (642-647 mm.)	Sp. rotation, α_D^{20}	N_D^{20}	Iodine no. (Hübl method)
1. <i>Artemisia tridentata typica</i>	0.92	0.9052	173.5	- 8.54	1.4689	168.0
2. <i>Gutierrezia sarothrae</i>	.33	.8678	157.5	+36.49	1.4741	304.4
3. <i>Juniperus Utahensis</i>	..	.8879	163.5	+56.36	1.4715	224.7
4. <i>Salvia lanceolata</i>	.32	.9254	185.5	+ 2.35	1.4771	110.9
5. <i>Thamnosma Texanum</i>	.05	.9593	128.0	+57.67	1.4737	119.4
6. <i>Tetrademia glabrata</i>	.12	.8522	163.0	1.4756	189.6
7. <i>Chrysothamnus graveolens</i>	.85	.8746	169.5	- 1.62	1.4842	184.1
8. <i>Chrysothamnus viscidiflorens elegans</i>	..	.8549	162.0	+20.67	1.4797	325.3
9. <i>Chrysothamnus nauseosus graphalodes</i>	.40	.8651	159.0	1.5080	...
10. <i>Chrysothamnus nauseosus viridulens</i>	.17	.9045	1.5008	...
11. <i>Chrysothamnus nauseosus hololeucus</i>	.18	.9797	160.5	1.5399	...
12. <i>Chrysothamnus nauseosus Mohavensis</i>	.16	.8924	126.0	1.4971	...

These oils, being mixtures, do not have very definite boiling points. There was no pressure correction made; the temperature at which the liquid in a flask to which a reflux condenser was attached freely boiled at the local barometric pressure was recorded as the boiling point.

The specific rotation and refractive index of the freshly distilled oil are recorded. Our observations show that these constants are subject to change when the oils are kept for some time, especially when exposed to light and air.

PURIFICATION OF ABIETIC ACID FROM ROSIN AND PREPARATION OF SOME OF ITS DERIVATIVES¹

BY C. C. KESLER WITH A. LOWY AND W. F. FARAGHER

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Rosin has not received as much scientific study as its importance in the industrial arts warrants. The annual value of rosin produced, of which somewhat less than sixty per cent. is exported, is approximately forty million dollars.

Rosin consists principally of organic acids commonly called abietic acid of the empirical formula $C_{20}H_{30}O_2$, and of a small per cent. of neutral material termed "resene." The resene seems to exert a decided influence on the reactivity of abietic acid. This is evidenced in a number of ways, but it has been especially noted in the esterification of the acid. No reaction or only a very small yield is at times obtainable when rosin is employed, but a satisfactory yield results when pure abietic acid is used. One of the chief difficulties encountered in research on this material has been obtaining a pure abietic acid.

The sodium complex salt method^{2,3,4,5} was employed in securing abietic acid from which the other derivatives were prepared. It is of interest to note that abietic acid and the normal sodium salt are soluble in alcohol, whereas the sodium complex salt ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$) is insoluble. Advantage is taken of this fact to effect purification, the resene remaining in solution being thereby separated from the abietic acid. This method, it is believed, has decided advantages over methods previously used that involve long and tedious crystallizations. Yields of 80% may be secured and the time required for the purification is greatly shortened. It has been noted that when abietic acid or its salts are in contact with the resene, oxidation is greatly facilitated. This has been definitely shown by preparing rosin soaps and noting the resulting changes in the presence and absence of resene. Extended crystallizations, especially in the presence of resene, give ideal opportunity for such oxidation.

Isomerization of rosin is essential for the formation of the complex

¹ The research described in this paper was carried out while Dr. Kesler was the incumbent of the Rosin Fellowship sustained in Mellon Institute by the Pine Institute of America (1924-1926), to which organization the authors are grateful for this support and also for the release of the work for publication. The present contribution is an abstract of a thesis presented by Dr. Kesler to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Aschan, *Ann.*, **424**, 117-33 (1921).

³ Maly, *Ann.*, **129**, 96 (1864).

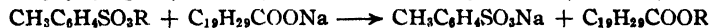
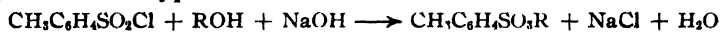
⁴ Freymy and Sievert, *Zeitschrift für die gesammten Naturwissenschaften*, **14**, 311 (1849).

⁵ *Bulletin de L'Institut du Pin*, March 15, 1926, p. 350.

salts as commercial amorphous rosin gives no such precipitate. The isomerization can be followed by the change in optical rotation. The original acid rotates light to the right, while the isomerized products give a negative rotation. Mineral acids effect this change. Aqueous or gaseous hydrochloric acid proves to be an effective isomerizing agent. The same result may be accomplished by heating to 250°.

As only a few esters of abietic acid are noted in the literature,^{6,7,8,9,10} a number of esters were prepared in order that the properties of these interesting neutral derivatives of rosin might be investigated. The use of dry hydrogen chloride as a catalytic agent was unsuccessful, so more energetic methods were sought. A number of methods have been used, and in the case of phenols the very reactive material phosgene was employed. The type reaction is $\text{RCOONa} + \text{R'ONa} + \text{COCl}_2 \longrightarrow \text{RCOOR'} + 2\text{NaCl} + \text{CO}_2$.

Hahn¹¹ gives a method for preparing esters of benzenesulfonic and *p*-toluenesulfonic acids. Gilman and Beaber¹² have also prepared a number of esters of *p*-toluenesulfonic acid. The alkyl *p*-toluenesulfonates obtained by this method, when mixed and heated with equimolecular quantities of sodium abietate dissolved in water, give the desired esters of abietic acid and sodium *p*-toluenesulfonate, which is water-soluble and may be recovered. The reaction proceeds very smoothly and often gives 95% yields. The type reaction is



The cost of reagents is not at all prohibitive to commercial production. It is possible to prepare not only aliphatic esters by this method but certain terpene esters as well.

The lower aliphatic esters are heavy, viscous oils of increasing boiling points with increasing weights. The specific gravities decrease as the series is ascended. The refractive indices check quite closely with the specific gravities and indicate that two double bonds are present in the molecule. The esters of the normal alcohols have higher boiling points than the corresponding *iso* compounds. A similar relation is also true in the case of specific gravities. The esters were all distilled at reduced pressures without decomposition.

Esters prepared with phenols could not be secured by any of the usual

⁶ Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1922, II, p. 494.

⁷ Virtanen, *Ann.*, **424**, 189 (1921).

⁸ Ruzicka and Meyer, *Helv. Chim. Acta*, **6**, 1077 (1923).

⁹ Ellis and Rabinovitz, *J. Ind. Eng. Chem.*, **8**, 406 (1916).

¹⁰ Kaufman and Friedebach, *Ber.*, **55**, 1508 (1922).

¹¹ Hahn, *Ber.*, **54**, 1531 (1921).

¹² Gilman and Beaber, *THIS JOURNAL*, **47**, 518 (1925).

methods of esterification. As a result, a new method was developed which involves the action of phosgene upon dry sodium phenolates and sodium abietate with the formation of sodium chloride and carbon dioxide. It is quite essential that the materials be finely powdered, well mixed and thoroughly dried. Pressure increased the yields. The method works very well for all phenols employed and is believed to be a general reaction. Esters prepared with phenols are semi-solids at room temperature and are darker in color than the aliphatic esters. This method also gives fair results with certain of the terpene alcohols, such as are found in pine oil. Both rosin and pine oil are commercial products and their union gives esters which should be of considerable practical value. The pine oil alcohols are quite difficult to esterify as certain of them, such as terpineol, are tertiary alcohols. The esters are insoluble in water, but soluble in the usual organic solvents. However, they are only slightly soluble in cold alcohol but more so when heated. The insolubility in alcohol decreases as the series is ascended.

The plasticizers or softeners used in the manufacture of nitrocellulose lacquers are an important industrial commodity. The amount of plasticizer varies from 40 to 60% of the nitrocellulose employed. Its purpose is to remain in the film, keeping it soft and pliable without greatly diminishing its strength. The softener should be non-volatile and neutral in character; it should be miscible with lacquer solvents and a solvent for nitrocellulose; it should be stable on aging in lacquer films. Some of the esters of abietic acid appear to have application in this industry.

Experimental

One kilogram of "G" grade rosin containing 91% abietic acid was isomerized either by passing a current of dry hydrogen chloride gas through the melted rosin with constant stirring for twenty minutes, or by adding 1% of hydrogen chloride in the form of commercial aqueous hydrochloric acid to a hot 33% alcoholic solution of rosin. This was boiled for fifteen minutes. Aqueous or alcoholic sodium hydroxide was added to neutralize completely the hydrochloric acid and enough more to neutralize one-fourth of the acid content of the rosin. Stirring was discontinued and the mixture allowed to cool. Seeding facilitates crystallization of the sodium complex salt ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$). The entire solution sets into a white, solid, sponge-like mass composed of small, needle-like crystals which may be pressed or centrifuged to remove the mother liquor. Without washing, the salt contained less than $\frac{1}{2}$ of 1% of resene. A single alcoholic wash gives a pure sodium complex salt ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$), melting at 177° . Regeneration of abietic acid with subsequent precipitation does not raise the melting point.

Twenty grams of the complex sodium salt ($C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$) gave the following titration and gravimetric values.

Anal. Calcd. for 2.540 *N* alkali: 19.2 cc. Found: 19.1. Calcd.: Na, 0.3739 g. Found: 0.3734, 0.3729.

The calculated amount of mineral or acetic acid was added to the complex sodium salt in order to free the abietic acid. It melted when dry at 166° . Recrystallization does not raise the melting point.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.47; H, 9.93. Found: C, 78.98; H, 10.33.

Sodium abietate was prepared by treating the pure complex sodium salt with sufficient alkali and slowly drying with constant stirring in an atmosphere of carbon dioxide. The small lumps were finely pulverized and dried in a vacuum oven at 100° for four hours. The acid formed by treating the dried sodium abietate with acetic acid has the properties of pure abietic acid. This method was employed for preparing sodium abietate in all subsequent experiments where it is used.

Ethyl Abietate ($C_{19}H_{29}COOC_2H_5$).—To one mole (324 g.) of dry sodium abietate, one mole (154 g.) of diethyl sulfate was gradually added and the reaction mixture slowly stirred on a steam-bath for two hours. It was cooled and extracted with benzene. Upon removal of the solvent, a viscous oil remained which is nearly odorless and possesses a light yellow color not removed by repeated distillation. The yield is 85% of the theoretical. Saponification number found: 170.1; calcd.: 169.6. The properties of the following esters are found in Table I.

Propyl Abietate ($C_{19}H_{29}COOC_3H_7$).—One mole of sodium abietate dissolved in 600 cc. of water was refluxed with one mole of *n*-propyl-*p*-toluenesulfonate with constant stirring for two hours. The reaction mixture was allowed to cool. The ester layer was washed with water and distilled. An 80% yield of light yellow, odorless oil was obtained. Saponification number found: 163.0; calcd.: 162.7.

Isopropyl Abietate ($C_{19}H_{29}COOC_3H_7$).—One mole of abietic acid was neutralized with 40 g. of sodium hydroxide in 600 cc. of water and heated until all the abietic acid was dissolved. Upon cooling, the soap set to a gel which was treated by the *p*-toluenesulfonate method as described above.

The following esters were also prepared by the *p*-toluenesulfonate method as described above.

n-Butyl abietate ($C_{19}H_{29}COOC_4H_9$); yield, 95%; saponification number found: 155.9; calcd.: 156.4.

*iso*Butyl abietate ($C_{19}H_{29}COOC_4H_9$); yield, 80%.

iso-Amyl abietate ($C_{19}H_{29}COOC_5H_{11}$); yield, 72%.

Allyl abietate ($C_{19}H_{29}COOC_3H_5$); yield, 45%.

Menthyl abietate ($C_{19}H_{29}COOC_{10}H_{19}$); yield, 65%.

Phenyl Abietate ($C_{19}H_{29}COOC_6H_5$).—One mole (116 g.) of carefully dried and powdered sodium phenolate was thoroughly mixed with one mole (324 g.) of well-dried and powdered sodium abietate. The mixture was placed in a glass tube in a well-ventilated hood and phosgene allowed to pass through the powder. No heat was applied but the heat of reaction was quite noticeable. A characteristic change to a resinous, viscous mass was noted and in one-half hour the reaction was complete. The reaction products were well washed with water and dilute alkali. The remaining semi-solid ester distilled at 330 – 333° at 4 mm., giving a dark-colored gum which did not become lighter in color by redistilling. The experiment was repeated in a bomb tube with liquid phosgene at room temperature and a yield of 87% was obtained. The specific gravity of the ester was 1.056 ($15^\circ/4^\circ$) and refractive index 1.5354. Upon saponification with 10% alkali and subsequent acidification, abietic acid crystals and phenol were again obtained.

The following esters were prepared by the phosgene method as described for phenyl abietate.

Hexalin abietate ($C_{19}H_{29}COOC_6H_{11}$); yield, 73%; saponification number found: 144.6; calcd.: 145.8.

m-Tolyl abietate ($C_{19}H_{29}COOC_7H_7$); yield, 78%.

α -Naphthyl abietate ($C_{19}H_{19}COOC_{10}H_7$); yield, 78%.

Terpineol abietate ($C_{19}H_{19}COOC_{10}H_{17}$).

Bornyl abietate ($C_{19}H_{19}COOC_{10}H_{17}$); yield, 75%.

Benzyl Abietate ($C_{19}H_{19}COOC_7H_7$).—One-fourth mole of abietic acid was dissolved in carbon tetrachloride with one-fourth mole of benzyl chloride. Twenty-five cc. of 40% sodium hydroxide was slowly added and then 25 cc. of water. The mixture was refluxed for three hours at which time the odor of benzyl chloride had disappeared. The ester was washed and the solvent removed by distillation. A yield of 85% was secured. Saponification number found: 141.7; calcd.: 142.8.

Cholesteryl Abietate ($C_{19}H_{19}COOC_{26}H_{49}$).—One-tenth mole of cholesterol was melted with one-tenth mole of abietic acid in the presence of zinc as a catalyst. After heating for two hours at 200°, a resin was obtained. The resin was dissolved in benzene and washed. The solvent was distilled off, leaving a resin which could not be distilled without decomposition. A yield of 94% was secured. Saponification number found: 83.6; calcd. 85.3. This ester was also obtained from cholesteryl chloride and sodium abietate. The cholesteryl chloride was made by treating cholesterol with sulfuryl chloride.

Cetyl Abietate ($C_{19}H_{19}COOC_{16}H_{33}$).—This ester was prepared by heating at 150° for six hours equal molecular quantities of cetyl iodide and sodium abietate. The reaction product was dissolved in benzene and washed. The recovered resin gives no test for halogen.

To determine the applicability of the esters of abietic acid as plasticizers, a number of films were prepared on a copper plate having a surface of mercury amalgam. A standard lacquer composition was prepared in which tricresol phosphate and dibutyl phthalate were used as the plasticizers. By substituting esters of abietic acid for the standard plasticizers, comparisons of the resulting films were made. A typical composition is as follows:

Substance	Per cent.	Substance	Per cent.
Nitrocellulose in ansol.	10	Butyl alcohol.	20
Ester gum.	5	Diethyl carbonate.	8
Esters of abietic acid.	5	Toluene.	32
Ansol.	20		

The solubility of the cellulose nitrate in the different esters, the flexibility and adhesion of the film and its strength and elasticity were especially noted. The results obtained indicate that abietic acid esters possess properties allowing their use wherever a neutral or softening effect is desired.

TABLE I
CONSTANTS OF ESTERS

Esters of abietic acid	B. p., °C.	Press., min.	M. p., °C.	Sp. gr. 15°/4°	Refrac- tive index
Methyl.	225-226	16	1.050	1.5344
Ethyl.	204-207	4	1.032	1.5265
<i>n</i> -Propyl.	237-240	4	1.015	1.5229
<i>iso</i> Propyl.	214-217	4	1.010	1.5200
<i>n</i> -Butyl.	247-250	3	1.014	1.5192

TABLE I (Concluded)

Esters of abietic acid	B. p., °C.	Press., mm. Hg	M p., °C.	Sp. gr. 15°/4°	Refrac- tive index
<i>iso</i> -Butyl	222-225	4		1.008	1.5171
<i>iso</i> -Amyl	254-257	4		1.001	1.5165
Allyl	282-285	5		1.024	1.5242
Phenyl	330-333	4		1.056	1.5354
Hexalin	299-302	4		1.061	1.535
<i>m</i> -Tolyl	310-313	5		1.039	
α -Naphthyl	290 (decomp)	2		1.116	
Terpineol	310 (decomp)	2		1.082	
Benzyl	294-297	4		1.036	1.551
Cholesteryl			122-125		
Menthyl			77-83 (softens)		
Bornyl			75-80 (softens)		
Cetyl			42		
Sodium complex abietate			177		
Abietic acid			166		

Summary

1. A method which is based on the formation of an acid salt of rosin has been employed for purifying rosin to obtain abietic acid in good yield. Some advantages of this method are indicated.

2. A number of new esters of abietic acid have been prepared and their properties determined (see Table I). Certain of these esters have commercial applications wherever a plasticizing or softening effect is desired.

3. A new method has been developed with phosgene for securing esters of phenols and esters with alcohols of the terpene family. It is believed to be a general reaction for such materials.

4. The value of esters of *p*-toluenesulfonic acid as esterifying reagents for preparing esters of abietic acid is shown.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

ORGANOBERYLLIUM HALIDES

BY HENRY GILMAN AND F. SCHULZE

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Introduction

Durand¹ has recently described the preparation of methylberyllium iodide by the action of finely-divided beryllium upon methyl iodide in ether, using a trace of mercuric chloride as a catalyst. Gilman² had previously found it impossible to prepare organoberyllium halides directly. More recently, Gilman and Schulze³ have prepared these organometallic halides by indirect methods starting with beryllium dialkyls.

We have now attempted to prepare these substances following Durand's method, but without success. By the use of revised directions, in particular prolonged heating at elevated temperatures, we have succeeded in preparing organoberyllium halides directly. The methylberyllium iodide we obtained was, contrary to Durand's experiences, very soluble in ether. His method of purification, by ether washing, should, therefore, have completely removed the compound leaving no organoberyllium iodide for analysis. Finally we have shown that the gas Durand obtained by the hydrolysis of his reaction product was presumably hydrogen and not methane. Accordingly, our unavoidable conclusion is that Durand's product was not methylberyllium iodide.⁴

Experimental Part

When Durand's directions for the preparation of methylberyllium iodide were carried out in detail (using 0.091 g., 0.01 mole, of beryllium and corresponding amounts of methyl iodide, mercuric chloride and ether) a small amount of gray material remained suspended in the ether and most of the metal rested unchanged on the bottom of the flask. After removal of the ether by slow evaporation, the residue was washed twice with anhydrous ether leaving the grayish material and unused metal. The residue was analyzed after displacing all the air by carbon dioxide. Hydrolysis by dilute hydrochloric acid gave 216.5 cc. instead of the calculated 224 cc. of gas. Analysis by explosion with oxygen showed the gas to be pure hydrogen, and there was no trace of carbon dioxide. Qualitative analysis proved the absence of iodine in the "reaction product."

¹ Durand, *Compt. rend.*, **182**, 1162 (1926).

² Gilman, *THIS JOURNAL*, **45**, 2693 (1923). References to all earlier work are contained in this article.

³ Gilman and Schulze, *J. Chem. Soc.*, 1927.

⁴ His analogies with the related beryllium diethyl and magnesium diethyl are based in large part on Cahours' work with these compounds and we have shown much of Cahours' work to be incorrect (see ref. 3 and Gilman and Schulze, *THIS JOURNAL*, **49**, 2328 (1927) for an account of magnesium diethyl).

The local reaction reported by Durand is undoubtedly independent of the presence of methyl iodide or any other of the alkyl and aryl halides tried by us. This was shown by a wide variety of experiments in which beryllium powder was treated with varying quantities of mercuric chloride in the presence of ether and with or without the addition of various RX compounds. A local reaction invariably took place between the metal and mercuric chloride and a light gray solid formed. Larger quantities of mercuric chloride gave increasing amounts of the gray solid and free mercury appeared to deposit on the beryllium, probably forming an amalgam. Undoubtedly, the only reaction that occurred was a simple displacement of the mercury by the beryllium, inasmuch as free mercury was formed and in several cases the liquid etherate of beryllium chloride was noted.

The small amount of mercuric chloride (0.1 g.) taken by Durand would use up an extremely small quantity of the beryllium (9.1 g. of beryllium being equivalent to 271.5 g. of mercuric chloride) so that his gas analysis would hardly be affected. It is obvious that treatment with dilute hydrochloric acid would liberate the same volume of gas, regardless of whether the metal was essentially unchanged or had formed a quantitative yield of methylberyllium iodide.

Temperature.—No methylberyllium iodide is formed when 0.091 g. (0.01 mole) of finely-divided beryllium,⁵ 1.4 g. (0.01 mole) of methyl iodide, 15 cc. of ether and a trace of mercuric chloride are shaken in a sealed test-tube at room temperature for one week.

Heating at 80–90° for fifteen hours was generally necessary to prepare appreciable quantities of the organoberyllium halide. The reaction product was a slightly turbid solution, resembling somewhat the solution of a Grignard reagent, although it was generally lighter in color than many RMgX solutions. The greater part of the metal invariably remained unattacked and rested on the bottom of the tube. In addition to the metal, there was usually present a small quantity of black material in the form of small scales or definite particles. This material was somewhat lighter than the metal, settling less rapidly when the tubes were agitated.

In many experiments the reagents were heated at 80–90° for periods in excess of fifteen hours and up to one week. Judging by the depth of the color test recommended by Gilman and Schulze⁶ for RMgX and some other organometallic compounds, there was no appreciable increase in yield with these extended periods of heating. Incidentally, these experiments served to show that prolonged heating did not destroy the organoberyllium compounds. Only a few experiments were carried out at higher temperatures and positive tests were obtained after heating to 150°.

Catalysts.—Mercuric chloride, used by Durand, gave the best results with all the alkyl and aryl halides that were investigated. The other mercuric halides may be used but they are not as satisfactory. Beryllium chloride is next to mercuric chloride in order of effectiveness. Mercury and iodine together, iodine and bromine are about

⁵ The beryllium used in this study was obtained from the Beryllium Corporation of America. Their analysis showed it to contain more than 99.5% of beryllium, with about 0.2% iron, 0.1% silicon and no aluminum.

⁶ Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

of equal value. It was disappointing to find that a finely-divided beryllium-copper alloy containing about 12% of copper and activated by heating with iodine in an evacuated, sealed tube gave but moderately successful results, inasmuch as Gilman, Schulze and Peterson⁷ found that a magnesium-copper alloy containing 12.75% of copper is superior to Baeyer's activated magnesium in the preparation of some Grignard reagents that are formed with difficulty.

Solvents.—Ethyl ether was the only solvent used and it was dried by a sodium-potassium alloy. When beryllium was heated with methyl iodide and mercuric chloride at 80–90° for one week with no ether present a light gray solid and clear liquid resulted. This reaction product gave a positive color test directly without the usual necessity of heating until fumes were evolved.^{8,9}

No reaction occurs when methyl and ethyl iodides are treated as above, but heated only for fifteen hours. Furthermore, beryllium with methyl or ethyl iodide, but no catalyst, showed no signs of having reacted after heating at 80–90° for several days. This is of interest in connection with Cahours' early work.^{4,9}

Preparation of Methyl- and Ethylberyllium Iodide.—In general, only small quantities of materials were prepared at one time because of the difficulty and danger involved in the heating of large volumes of ether in sealed tubes. Convenient reaction vessels may be prepared from the commercially available small, heavy sealed bottles used for the shipment of low-boiling liquids.

About 0.5 g. of powdered beryllium, 0.2–0.5 g. of mercuric chloride, 5 cc. of the organic halide and 25 cc. of ether are placed in the bottle. The neck of the bottle is drawn down to a fine capillary, small enough so that particles of beryllium cannot pass through, and the end of the capillary is sealed. The bottle is placed inside a can, which acts as a shield in case of explosion, and this is set on a steam hot-plate. After maintaining a temperature of 80–90° for at least fifteen hours, the bottle is cooled and its capillary end is first inserted in a 50cc. Erlenmeyer flask and then broken by pressing it against the walls of the flask. The high pressure in the bottle forces the liquid out and the unused metal is retained by the capillary. It is advisable to wrap the bottle in a towel in order to guard against the danger of an explosion. If the bottle has a sufficiently long neck, it may be used again by adding a fresh portion of alkyl halide, ether and mercuric chloride to the residual metal, then sealing and heating as before.

Preparation of Other Organoberyllium Halides.—Ethylberyllium bromide and *n*-butylberyllium iodide were prepared in the presence of ether, with mercuric chloride or beryllium chloride or free bromine as a catalyst. Here it was necessary to heat at 80–90° for fifteen hours.

Phenylberyllium iodide gave a positive test when prepared in the presence of mercuric chloride after heating at 80–90° for fifteen hours. This experiment was not duplicated in another run. However, the phenyl-

⁷ A preliminary account of this work was presented at the Philadelphia, 1926, meeting of the American Chemical Society. The alloy has been referred to in several later studies. (See Gilman and Harris, *THIS JOURNAL*, 49, 1827 (1927), ref. 10.)

⁸ Methylberyllium iodide gives a positive color test when the solution is allowed to stand for ten to fifteen minutes with Michler's ketone before hydrolysis and the addition of the iodine-glacial acetic acid solution.⁶ The beryllium dialkyls, formed by heating alkylberyllium halides, give a color test at once. The slower reaction of alkylberyllium halides is not unique, inasmuch as some tertiary alkylmagnesium halides also require up to five minutes' standing before a satisfactory color test is obtained. (See Gilman and Schulze, *Bull. soc. chim.*, 1927.)

⁹ Cahours, *Ann. chim. phys.*, [3] 58, 5 (1860).

beryllium iodide was readily prepared by heating at a more elevated temperature (150 or 175°) with either mercuric chloride or beryllium chloride as a catalyst.

Tert.-butyl chloride and bromide appeared to have reacted when heated at 80–90° for fifteen hours with mercuric chloride as a catalyst. However, the products in both cases gave negative tests.⁸ Under like conditions, benzyl bromide and *n*-butyl chloride showed no evidence of reaction.

Reactions of Alkylberyllium Halides.—All of these compounds are decomposed by water, with the formation of the corresponding hydrocarbon.

The ethereal solutions do not fume in the air. However, by driving off the ether a liquid residue results and this on further heating gives off dense white fumes, probably of beryllium oxide. This application of heat by a small luminous flame converts the alkylberyllium halide to a beryllium dialkyl. Beryllium dimethyl¹³ was definitely identified in this manner when methylberyllium iodide was heated. The following equilibrium is quite probable under certain conditions



inasmuch as alkylberyllium halides are formed when beryllium dialkyls are treated with a beryllium halide. Some experiments on the heating of RMgX compounds indicate that the same may be true with organomagnesium compounds.

When carbon dioxide was bubbled through an ethereal solution of methylberyllium iodide for three hours, the solution still gave a positive test and no acetic acid was found after hydrolysis.

The color test with Michler's ketone is developed only after ten to fifteen minutes' standing prior to hydrolysis.⁸ Beryllium dialkyls give the test at once.

Acetanilide is formed from methylberyllium iodide and phenyl isocyanate. This is a standard reaction for organomagnesium, calcium and barium halides as well as for beryllium and magnesium dialkyls.

In general, the alkylberyllium halides are less reactive than the beryllium dialkyls and the RMgX compounds.

Summary

Organoberyllium halides could not be obtained directly by procedure given in the literature but were produced in the presence of various catalysts by prolonged heating in sealed tubes at temperatures up to 150°.

The properties of the methylberyllium iodide were markedly different from those given by Durand, so that our conclusion is that his product was not this substance.

Methyl- and ethylberyllium iodides, ethylberyllium bromide, *n*-butyl-

beryllium iodide and phenylberyllium iodide have been prepared and their reactions investigated.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE UNIVERSITY OF ILLINOIS]

THE PREPARATION AND BASE STRENGTHS OF SOME AMINES

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The measurements here recorded were made for the purpose of supplementing existing data on the base strengths of amines. The data obtained are summarized in the following table.

TABLE I
DATA ON BASE STRENGTHS OF AMINES

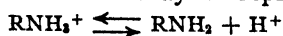
Formula	Neutral. equiv., calcd.	Neutral. equiv. found	$K_{\text{hydr.}} \times 10^{10}$ $t = 25^\circ$	$K_B \times 10^5$
$(\text{C}_6\text{H}_5\text{NH}_2)$	$(2.17 \times 10^5)^1$	$(4.6 \times 10^{-5})^1$
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	107.1	107.3	4.26	2.35
$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_2$	121.1	...	1.48	6.78
$\text{C}_6\text{H}_5(\text{CH}_2)_3\text{NH}_2$	135.1	135.1	0.63	15.9
$\text{C}_6\text{H}_5(\text{CH}_2)_4\text{NH}_2$	149.2	149.4	.40	24.8
$\text{C}_6\text{H}_5(\text{CH}_2)_5\text{NH}_2$	163.2	163.1	.33	30.6
$o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$	121.1	121.5	5.89	1.70
$m\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$	121.1	121.8	4.24	2.40
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$	121.1	121.1	3.98	2.55
$o\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{NH}_2$	137.1	137.9	1.81	5.56
$m\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{NH}_2$	137.1	137.5	6.46	1.56
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{NH}_2$	137.1	137.2	3.10	3.22
$\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_3$	121.1	121.3	2.63	3.80
$\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_2\text{CH}_3$	135.1	134.8	2.10	4.75
$\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$	149.1	149.1	2.40	4.18
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NHCH}_3$	135.1	135.6	0.75	13.9

The first five amines constitute a series of the type $\text{R}(\text{CH}_2)_x\text{NH}_2$ where R is the negative phenyl group. The data are of some interest in connection with the transmission of polar effects through a chain of atoms. Data are available on several similar series of acids and it is well known that the effect of the substituent R on the dissociation of the acid diminishes continuously with the increasing values of x . Where R is $-\text{CH}=\text{CH}$, however, the dissociation constants appear to alternate with increasing values of x . Data on the acids $\text{C}_6\text{H}_5(\text{CH}_2)_x\text{COOH}$ are not available, but since phenyl contains the group $\text{C}=\text{C}-$, there was some possibility

that alternation might be observed in the series of amines here under discussion.

¹ Lunden, *Z. physik. Chem.*, **54**, 532 (1906).

The hydrolysis of an amine salt may be represented by the equation



and the hydrolytic constant is defined by the expression

$$\frac{[\text{RNH}_2][\text{H}^+]}{[\text{RNH}_3^+]} = K_{\text{hydr.}}^2$$

The hydrolytic constant of an amine then furnishes a measure of the tendency of a hydrogen ion to leave the nitrogen atom, and there should be a parallelism between the dissociation constants of acids and the hydrolytic constants of the corresponding bases.³ The amines, however, seem to present a simpler picture than the acids, for apart from the fact that there is in these a greater distance between R group and the proton which dissociates, the relatively greater complexity of the carboxyl group may permit a more complex behavior. Hantzsch⁴ has in fact advanced definite experimental evidence for concluding that two distinct types of carboxyl groups exist.

In regard to the amines $\text{C}_6\text{H}_5(\text{CH}_2)_x\text{NH}_2$, the data summarized above show that the values of $K_{\text{hydr.}}$ diminish continuously as the values of x increase. This decrease though continuous is not quite regular, and the data do not fit well the $1/3$ rule of Derick⁵ or an equation of the type suggested by Simms.⁶

It is interesting to compare the data on these amines with those on the reactivities of the corresponding chlorides as measured by Conant and Kirner.⁷ The effect of the phenyl group does not here diminish continuously as the distance from the halogen atom increases, but in the first members of the series there is evidence of alternation. It is evident

² It is of course implied in this that the conditions are such that the concentrations are equal to the activities.

As Brönsted has pointed out (Brönsted, *Rec. trav. chim.*, [4] **42**, 718 (1923)) the use of the equation $\text{NH}_4^+ + \text{HOH} \longrightarrow \text{NH}_4\text{OH} + \text{H}^+$ to represent the hydrolysis of an ammonium salt rests on an unnecessarily complicated conception. According to Brönsted's idea ammonium chloride reacts acid because the ammonium ion is an acid. The question of the extent to which the base strength of ammonia is determined by each of the reactions $\text{NH}_3 + \text{HOH} \rightleftharpoons \text{NH}_4\text{OH}$ and $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ becomes immaterial when Brönsted's more general definition of a base is used. Incidentally the octet theory leads to a similar conclusion, since the most obvious manner of

representing ammonium hydroxide is $\text{H}:\ddot{\text{N}}:\text{H}$ $\begin{smallmatrix} \text{H} \\ \vdots \\ \text{O} \\ \vdots \\ \text{H} \end{smallmatrix}$ and the weakness of ammonia as a base is accounted for by supposing that the equilibrium lies in favor of $\text{NH}_3 + \text{H}_2\text{O}$, the formation of these involving merely the transfer of a hydrogen ion from the ammonium ion to the hydroxyl ion.

³ See in this connection Hixon and Johns, *THIS JOURNAL*, **49**, 1786 (1927).

⁴ Hantzsch, *Ber.*, **50**, 1422 (1917).

⁵ Derick, *THIS JOURNAL*, **33**, 1181 (1911).

⁶ Simms, *ibid.*, **48**, 1251 (1926).

⁷ Conant and Kirner, *ibid.*, **46**, 232 (1924).

that those qualities of structure which govern the base strength of amines are not the same as those which govern the tendencies of the chlorides to undergo metathesis. Of the two reactions the hydrolysis of the amine salt is evidently the simpler, since it involves merely the reversible separation of a proton. Concerning the mechanism of the reaction of an alkyl halide nothing whatever is known. If the term polarity is to be used, it seems much more appropriate to use it in connection with the hydrolysis of the amine salt, a reaction involving the loss of an elementary positive charge, than in connection with the reactions of an alkyl chloride which proceed in a fashion at present wholly obscure.

The reasons which Conant, Kirner and Hussey⁸ found for concluding that variations in the reactivities of chlorides could not be accounted for solely in terms of polarity find additional support in the above argument.

The data on the *o*-, *m*- and *p*-methyl- and methoxylbenzylamines indicate that the effects of these substituents are slight and vary in an irregular fashion with changes of position.

Of the secondary amines two have previously been measured by Bourgeaud and Dondelinger.⁹ For methylbenzylamine these writers give $K_B = 7.95 \times 10^{-8}$, and for ethylbenzylamine 5.04×10^{-8} . The values indicated in the above table are in one case 500 and in the other 1000 times as great as these. Although some difficulty was experienced in getting sharply consistent readings on these amines, the writers are inclined to suppose that the values given by Bourgeaud and Dondelinger must be seriously in error. These values are of an entirely different order of magnitude from those of the corresponding primary and the analogous tertiary amines, and imply an effect due to the introduction of a simple alkyl group quite unprecedented. The measurements of these investigators were evidently carried out with great care but their method appears to be fundamentally untrustworthy. They measured, with the aid of the hydrogen or quinhydrone electrode, the *P_H* of solutions of the pure hydrochlorides of the amines. Their solutions were therefore very inadequately buffered; and slight traces of impurities or quite possible variations in the compositions of the purified hydrochlorides would suffice to render their results meaningless.

As the table shows, the amines $C_6H_5CH_2NHR$ where R is methyl, ethyl and *n*-propyl are just about twice as strong bases as benzylamine, and a similar relationship holds between methylphenethyl- and phenethylamine.

Benzylamine has been measured by Bredig by the conductivity method¹⁰ and the value which he assigns to it ($K_B = 2.4 \times 10^{-5}$) agrees with that found in the present investigation.

⁸ Conant, Kirner and Hussey, *THIS JOURNAL*, 47, 492 (1925).

⁹ Bourgeaud and Dondelinger, *Bull. soc. chim.*, 37, 282 (1925).

¹⁰ Bredig, *Z. physik. Chem.*, 13, 191 (1894).

Method Used in Measuring the Base Strengths.—The method used was to determine the P_H of solutions of the base in water to which a definite fraction of an equivalent amount of hydrochloric acid had been added. This fraction was usually $\frac{1}{2}$ but sometimes $\frac{2}{3}$ or $\frac{3}{4}$. This method is satisfactory only if the amine is appreciably soluble in water and quite pure, and if the composition of the solution is definitely known. The purified amine was distilled in a vacuum in a small Claisen flask with a sealed-in thermometer, etc., and was collected with the aid of a bifurcated adaptor in two test-tubes. One of these contained a number of small bulbs weighed and marked standing on their capillary tips. The middle fraction of the amine was collected in this tube and when air was admitted to the receiver the bulbs were automatically filled. The amine was thus preserved from contact with moisture and carbon dioxide. The bulbs were immediately sealed off and weighed. To control the purity some of the tubes were broken under water and the solutions titrated using a suitable indicator (usually methyl red). To prepare a solution for measurement the bulb containing a known amount of the amine was placed in a glass-stoppered bottle, $\frac{1}{2}$ an equivalent of 0.01 N hydrochloric acid added and the stoppered flask shaken vigorously to break the thin bulb. This method of operation protected the amine against exposure to the air.

The electrodes were usually palladized platinum foils, though platinized platinum foils were also tried and in some cases wires were used. The hydrogen electrode was connected to 0.1 N and saturated calomel electrodes through a saturated potassium chloride salt bridge. Boundary potentials were disregarded. The two calomel electrodes were frequently compared with each other and with a hydrogen electrode in a standard 0.05 M potassium hydrogen phthalate buffer. The cells were immersed in a water-bath, the temperature of which was regulated by hand to $25 \pm 0.2^\circ$. For measurement of potentials a Leeds and Northrup Student Potentiometer was used. Measurements were made on three or more samples of each amine, with at least two fresh electrodes on each solution and usually at two different dilutions. In each case a series of readings was made against the 0.1 N calomel ($E = 0.3370$) and the saturated calomel ($E = 0.2458$) electrode. The agreement of the various series of readings was usually quite good, although some difficulty was experienced in getting sharply consistent results with the secondary amines. With a similar series of tertiary amines no consistent readings could be obtained.

Preparation of the Amines.—All of the amines measured in this work with the exception of one have been previously described. The following notes may, however, be of interest to those who have to prepare similar compounds.

The amines of the series $C_6H_5(CH_2)_nNH_2$ with the exception of benzylamine were prepared by the reduction of the corresponding nitriles. As von Braun has shown¹¹ this method, which gives poor yields in the preparation of phenethylamine, works very well for the higher members of the series. Commercial phenethyl alcohol was the starting point in the preparation of phenethyl cyanide. γ -Phenyl-*n*-propyl alcohol was prepared by the catalytic reduction of cinnamic aldehyde. This provided the starting point for the synthesis of phenylpropyl cyanide.

δ -Phenyl-*n*-butyl alcohol was prepared from β -phenethyl magnesium bromide by the action of ethylene oxide. This method has been used with satisfactory results in passing from RBr to RCH_2CH_2OH in a number of cases. In a small run this method gave a yield of 50% of the phenylbutyl alcohol, but in larger runs the yields were still poorer and the product required repeated careful fractionation. Although further study might increase the yields, this method cannot at present be recommended for obtaining compounds of the series $C_6H_5(CH_2)_n-$.

The substituted benzylamines were all prepared by the catalytic reduction of the appropriate nitriles or oximes, using acetic anhydride as the solvent. This method yields the acetyl derivative of the primary amine and avoids the formation of any secondary amine.¹² Hydrolysis of the amide then yields pure primary amine. The details of the preparation of *o*- and *p*-methylbenzylamines have already been described. The preparation of *m*-methylbenzylamine proceeds smoothly in the same fashion.

***p*-Anisylamine.**—The reduction of 0.1 mole of anisaldoxime in 40 cc. of acetic anhydride was complete in four hours using 0.1 g. of catalyst. The yield of the crude amide was quantitative. On crystallization from alcohol, it melted at 95.5–97°. The amide was hydrolyzed by boiling with 6 *N* hydrochloric acid for 24 hours. Some of the amide was transformed into a gum in this process and the yield of *p*-anisylamine (b. p. 132.8 to 134° at 33 mm.) was rather poor.

As has been previously pointed out the hydrolysis of benzylacetamide and substituted benzylacetamides is a slow process, although the reaction is much more rapid with hydrochloric acid than with alkalis. The presence of the methoxyl groups, however, complicates the hydrolysis by hydrochloric acid, and with the corresponding *o*- and *m*-compounds, methyl alcoholic sodium hydroxide at high temperature was used with much more satisfactory results.

Acetyl-*m*-methoxybenzylamine.—*m*-Anisic nitrile was prepared in good yield from *m*-anisidine by the Sandmeyer reaction; a colorless liquid, b. p. 111–112° at 12–13 mm. It readily crystallizes in an ice-bath to a mass of long needles. Reduction of the nitrile in acetic anhydride solution by the method already described yielded acetyl-*m*-methoxybenzylamine; b. p. 191–198° at 11 mm.; m. p. 58.5–59° (from ether and petroleum ether).

Anal. Calcd. for $C_{10}H_{13}O_2N$: N, 7.82. Found: 7.62

***m*-Methoxybenzylamine.**—The amide was hydrolyzed by heating for seven hours with methyl alcoholic sodium hydroxide in a sealed tube at 140–150°. The solution was steam distilled, the distillate neutralized with hydrochloric acid, evaporated to dryness, treated with sodium hydroxide, etc. The amine was obtained as a colorless liquid; b. p. 131° at 26 mm., 140° at 37 mm.

Neutral equivalent. Calcd. for $C_8H_{11}ON$: 137.1. Found: 137.5.

The hydrochloride of this amine has been described by Curtius.¹³

Acetyl-*o*-methoxybenzylamine.¹⁴—This was prepared in the same way as the *m*-

¹¹ Von Braun, *Ber.*, **44**, 2869 (1911).

¹² Carothers and Jones, *THIS JOURNAL*, **47**, 3051 (1925).

¹³ Curtius, *J. prakt. Chem.*, [2] **85**, 406, 436 (1912).

¹⁴ Previously prepared by Goldschmidt and Ernst, *Ber.*, **23**, 2740 (1890).

compound, b. p. 176–178 at 8 mm.; white needles from benzene and dry ether, m. p. 95–96°. It is practically insoluble in dry ether.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.04; H, 7.32; N, 7.82. Found: C, 67.27; H, 7.59; N, 7.71.

o-Methoxybenzylamine¹⁴ was prepared by hydrolysis of the amide; b. p. 127–28° at 30 mm.

Anal. Calcd. for $C_8H_{11}ON$: N, 10.22. Found: 10.07.

Neutral equivalent. Calcd.: 137.1. Found: 137.9.

The secondary amines were prepared from the corresponding primary amines by transformation into the *p*-toluenesulfonyl derivatives, alkylation and hydrolysis. Benzyl- and β -phenethylamines are much more readily acylated than aromatic amines. Hence, when the usual procedure of employing a 50% excess of the sulfonyl chloride is followed, considerable disulfonyl derivative is formed. The yields are therefore better if only 10–20% excess of the *p*-toluenesulfonyl chloride is used. The sulfonamides were prepared by adding a benzene solution of *p*-toluenesulfonyl chloride to an ice-cold solution of the amine in aqueous alkali. Afterward the mixture was heated on a steam-bath for two hours, the benzene distilled off and the residue acidified.

As the writer has previously stated, the benzenesulfonyl and *o*-toluenesulfonyl derivatives of benzylamine, β -phenethylamine, etc., are not soluble in aqueous alkali, statements in the literature to the contrary notwithstanding. It was found, however, that these amides are soluble in aqueous alcoholic sodium hydroxide (33% water, 66% alcohol). The use of this solvent made it possible to separate the *p*-toluenesulfonyl derivative from the di-*p*-toluenesulfonyl derivative and so to obtain the former in a state of purity.

This solvent was also found to be the best medium for the alkylation of the amines. Methyl iodide was found to be a much better methylating agent for these compounds than dimethyl sulfate, and ethyl bromide was better than diethyl sulfate. The alkylated *p*-toluenesulfonamides were freed from any unalkylated material by crystallizing them first from the alcoholic sodium hydroxide, in which the unalkylated material is soluble. This precaution was necessary because the alkylation was never quite complete and the separation of unalkylated material by the usual solvents required repeated crystallization. The alkylated amides were crystallized to constant melting point and then hydrolyzed in the usual fashion by heating in sealed tubes to 180° with concd. hydrochloric acid.

Sulfonamides

N-Methyl-N-benzyl-*p*-toluenesulfonamide, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCH}_3\text{CH}_2\text{C}_6\text{H}_5$, hexagonal leaflets from alcohol, m. p. 94.4–94.8°.

Anal. Calcd. for $C_{18}H_{17}O_2NS$: S, 11.62. Found: 11.62, 11.40.

N-Ethyl-N-benzyl-*p*-toluenesulfonamide, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_2\text{H}_5\text{CH}_2\text{C}_6\text{H}_5$, needles from alcohol, m. p. 49–50°.

Anal. Calcd. for $C_{18}H_{19}O_2NS$: S, 11.08. Found: 11.11, 11.20.

N-Propyl-N-benzyl-*p*-toluenesulfonamide, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NC}_3\text{H}_7\text{CH}_2\text{C}_6\text{H}_5$, m. p. 46–47°.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: S, 10.57. Found: 10.60, 10.60, 10.73.

N-Methyl-N- β -phenethyl-*p*-toluenesulfonamide, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$, white crystals from ether-petroleum ether, m. p. 44–45°.

Anal. Calcd. for $C_{18}H_{21}O_2NS$: S, 11.08. Found: 11.04.

N-Di-*p*-toluenesulfonylbenzylamine, $(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2)_2\text{NCH}_2\text{C}_6\text{H}_5$, m. p. 161°.

Anal. Calcd. for $C_{21}H_{21}O_4NS_2$: S, 15.44. Found: 15.38.

N-Di-*p*-toluenesulfonyl- β -phenethylamine, $(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2)_2\text{NCH}_2\text{CH}_2\text{C}_6\text{H}_5$, m. p. 101°.

Anal. Calcd. for $C_{22}H_{23}O_4NS_2$: S, 14.94. Found: 14.93.

Summary

Data are presented on the preparation and on the base strengths of some amines.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF THE HYDROCARBON $C_{17}H_{18}$ OBTAINED BY THE DEHYDRATION OF *TERT*-BUTYLDIPHENYL-CARBINOL

BY DOROTHY E. BATEMAN¹ WITH C. S. MARVEL

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Some time ago Schlenk and Racky² reported the preparation of tetraphenyldi-*tert*-butylethane and asserted that this product was a stable hydrocarbon which did not show any of the characteristics of the hexaarylethanes. The recent work of Conant and his students³ on derivatives of dixanthyl has shown that certain aliphatic groups substituted for the hydrogens of what might be considered the ethane carbons in dixanthyl have almost as great a tendency to cause dissociation into free radicals as do phenyl groups in these positions. It has been shown that di-*sec*-butyl-dixanthyl is dissociated to about the same degree as diphenyldixanthyl. One might expect from analogy then that a *tert*-butyl group would have a strong tendency to produce dissociation. It would appear that the compound described by Schlenk needs to be reinvestigated, especially since his conclusions rest on rather incomplete experimental results.

In reviewing the subject in the literature it was found that Schlenk prepared diphenyl-*tert*-butylmethyl chloride from diphenyl-*tert*-butyl carbinol and acetyl chloride and obtained a product which melted at

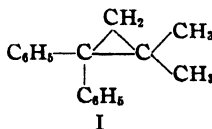
¹ This communication is an abstract of a thesis submitted by Dorothy E. Bateman in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in Chemistry, at the University of Illinois.

² Schlenk and Racky, *Ann.*, **394**, 202, 211, 212 (1912).

³ (a) Conant and Sloan, *This Journal*, **47**, 572 (1925); (b) *ibid.*, **47**, 3068 (1925); (c) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

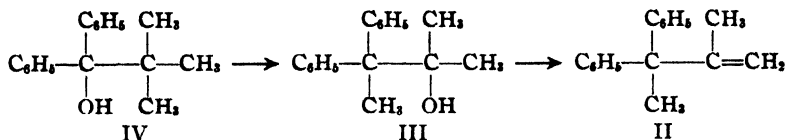
103–106°. About the same time Mme. Ramart-Lucas⁴ prepared this carbinol and obtained from it two isomeric chlorides, one melting at 71–72° and the other at 108–109°. The lower-melting chloride on hydrolysis gave the original carbinol and must have had the corresponding structure. It was further observed that the carbinol was easily dehydrated to give a hydrocarbon $C_{17}H_{18}$ which would add hydrogen chloride to give the higher-melting chloride mentioned above.

The structure of the hydrocarbon was studied by Mme. Ramart-Lucas.⁵ Several structures were suggested and disproved. Oxidation of the compound produced benzophenone, acetophenone and an acid which melted at 172–173° and to which from analyses the empirical formula $C_{17}H_{18}O_2$ was given. The structure which was favored seemed to be that of diphenyl-1,1-dimethyl-2,2-cyclopropane (I) which contained the cyclo-

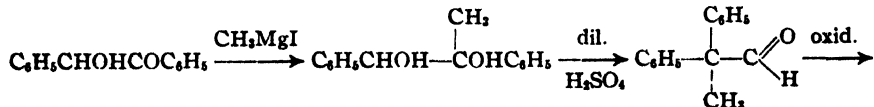


propane ring. However, the above formula does not explain the formation of acetophenone as an oxidation product and it is difficult to conceive of its oxidation to an acid, $C_{17}H_{18}O_2$.

In order to draw any conclusions concerning the work of Schlenk, it seemed necessary first to establish the structure of this unsaturated hydrocarbon and of the higher-melting chloride which was used in his experiments. The structure for the hydrocarbon which seemed most probable in advance was that of diphenyl-2,3-methyl-2-butene-1 (II), which would be the dehydration product of the carbinol (III) that would be formed if the original carbinol, *tert.*-butyldiphenylcarbinol (IV), were to undergo a Wagner rearrangement.

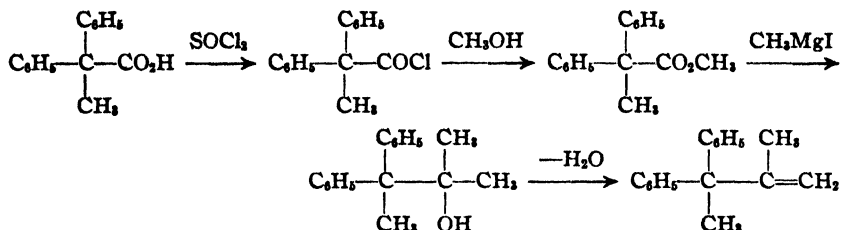


In order to test this prediction, a sample of diphenyl-3,3-methyl-2-butene-1 was prepared by the following series of reactions



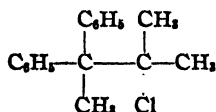
⁴ Ramart-Lucas, (a) *Compt. rend.*, 154, 1088 (1912); (b) *Ann. chim. phys.*, [8] 30, 367, 390 (1913).

⁵ Ref. 4 b, p. 406.



The diphenylmethylacetaldehyde was prepared from benzoin as described by Tiffeneau and Dorlencourt⁶ and was oxidized with alkaline permanganate solution to diphenylmethylacetic acid. The esterification of this acid and the reaction of the ester with the Grignard reagent were carried out in the usual manner. The carbinol was not isolated but was dehydrated directly.

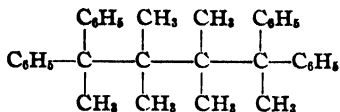
The hydrocarbon obtained in this way agreed in all of its properties with the one obtained by the dehydration of *tert.*-butyldiphenylcarbinol. In order to complete the identification, dry hydrogen chloride was added to both samples and a chloride melting at 102–106° was obtained in each case. There can be no further question concerning the constitution of the hydrocarbon. The higher-melting chloride obviously has the formula



The structure thus established for the hydrocarbon explains how both acetophenone and benzophenone can be obtained on oxidation. However, this compound could not give a seventeen carbon atom acid on oxidation. It might be expected to give some diphenylmethylacetic acid. The acid obtained by Mme. Ramart-Lucas melted at 172–173°, which is the melting point of diphenylmethylacetic acid. Some difficulty was encountered in attempting to duplicate the chromic acid oxidation of the hydrocarbon. However, ozone easily oxidized it to the ketone, diphenylmethylacetone, which on oxidation with sodium hypobromite solution gave diphenylmethylacetic acid melting at 174°. This acid is identical with the sample prepared by the oxidation of diphenylmethylacetaldehyde. There seems to be very little question that the acid previously thought to have the formula $\text{C}_{17}\text{H}_{18}\text{O}_2$ in reality has the composition $\text{C}_{15}\text{H}_{14}\text{O}_2$.

Since in his work Schlenk² used the chloride melting at 106° in his Würtz reaction to prepare a hexa-substituted ethane, it is quite obvious that he did not obtain tetraphenyl-di-*tert.*-butylethane but probably a hydrocarbon of the structure.

⁶ Tiffeneau and Dorlencourt, *Ann. chim. phys.*, [8] 16, 254 (1909).



A few attempts to couple the lower-melting chloride to give an ethane produced only the unsaturated hydrocarbon described before.

Experimental Part

***Tert.*-Butyldiphenylcarbinol.**—The method of Schlenk⁷ was used for this preparation. From 325 g. of phenylmagnesium bromide in 1 liter of dry ether and 114 g. of ethyl trimethylacetate there was obtained 135 g. of carbinol; b. p. 148–150° at 2.5 mm.; n_D^{20} 1.5748. The constants given by Mmc. Ramart-Lucas⁸ are n_D^{26} 1.57306; b. p. 178–180° at 11 mm.

Dehydration of *Tert.*-Butyldiphenylcarbinol.—In attempting to prepare the bromide from the carbinol, 24 g. of the latter was dissolved in 160 cc. of dry benzene and treated with 24 cc. of acetyl bromide. The mixture was allowed to stand for about 24 hours. The benzene was removed under reduced pressure and the residue distilled at about 3–3.5 mm. At this pressure the product boiled at 125–128°; d_4^{20} 1.0007; n_D^{20} 1.5730; M_D 73.03. The physical constants reported previously⁹ are d_4^{26} 1.0031; N_D^{26} 1.57589; observed M_D 73.23.

A more convenient method of dehydration was found. Sixty g. of the carbinol and a few grams of *p*-toluenesulfonic acid were placed in a small flask and heated on a boiling water-bath for about two hours. The mixture was treated with ether and the *p*-toluenesulfonic acid was removed by washing with dilute sodium carbonate solution and water. The ether solution was dried over sodium sulfate, filtered and evaporated. The residue was distilled under reduced pressure. The yield was 45 g. (81% of the theoretical amount) of hydrocarbon boiling at 125–128° at 3–3.5 mm.

Diphenylmethylacetic Acid.—Diphenylmethylacetaldehyde was prepared according to the directions of Tiffeneau and Dorlencourt.⁶ Benzoin and methylmagnesium iodide gave methylidihydrobenzoin in about 75% yields. This compound on rearrangement by boiling with 20% sulfuric acid solution gave diphenylmethylacetaldehyde in 60–70% yields.

In a flask fitted with a reflux condenser and mechanical stirrer were placed 136 g. of the aldehyde and a solution of 220 g. of potassium permanganate and 90 g. of sodium carbonate in 800 cc. of water. The mixture was refluxed with stirring until the color of the permanganate solution had disappeared. The solution was filtered to remove the manganese dioxide, extracted with ether to remove indifferent substances and then acidified with sulfuric acid. On filtering and drying, 80 g. of the acid was obtained. This was purified by recrystallization from 95% alcohol. The acid thus obtained weighed 61.5 g., melted at 172–174° and gave a neutral equivalent of 227.4 as compared with the calculated value, 226.

Methyl Diphenylmethylacetate.—A mixture of 59 g. of diphenylmethylacetic acid and 41 g. of thionyl chloride was refluxed on a steam-bath until solution was complete and no more sulfur dioxide and hydrogen chloride were being evolved. The excess thionyl chloride was removed by heating the reaction mixture under reduced pressure on a water-bath. About 20 g. of absolute methyl alcohol was added to the residue and the solution was refluxed for about four hours. It was then dissolved in ether and the

⁷ Ref. 2, p. 211.

⁸ Ref. 4 b, p. 367.

⁹ Ref. 4 b, p. 391.

solution was washed with sodium carbonate solution and water. The ether solution was dried over sodium sulfate, filtered and evaporated. The residue was distilled under reduced pressure and the portion boiling at 149–152° at 3 mm. was collected. The yield of ester was 46.5 g. (70% of the theoretical amount). It was a viscous liquid; n_D^{20} 1.5691; d_4^{20} 1.1206; M_D , calcd., 70.43; obs., 70.13.

Anal. Subs., 0.2030: CO₂, 0.6018; H₂O, 0.1220. Calcd. for C₁₈H₁₈O₂: C, 80.0; H, 6.67. Found: C, 80.89; H, 6.72.

Diphenyl-3,3-methyl-2-butene-1.—To 15 g. of magnesium turnings and 400 cc. of dry ether was added 90 g. of methyl iodide. When the Grignard reagent was formed, 45 g. of methyl diphenylmethylacetate was added, the mixture was allowed to stand for several hours and then refluxed on a water-bath for about one hour. The solution was treated with ammonium chloride solution to decompose the excess Grignard reagent and to dissolve the basic magnesium salts. The ether layer was separated and the aqueous layer was extracted with two small portions of ether. The ether solutions were combined, the ether was evaporated and the residual oil treated with about 5 g. of *p*-toluenesulfonic acid and heated to 125° for about 10 to 15 minutes. It was then dissolved in ether and the acidic material removed by washing the solution with dilute sodium carbonate solution. The ether was evaporated and the residue was refluxed with alcoholic potassium hydroxide solution to hydrolyze any unreacted ester. This solution was evaporated until the alcohol was removed and then water was added. The insoluble oil was collected in ether, the ether solution dried over sodium sulfate, filtered and evaporated. The residue was fractionated under reduced pressure and the main fraction collected at 132–133° at 4.5 mm.

Anal. Subs., 0.2067: CO₂, 0.6903; H₂O, 0.1488. Calcd. for C₁₇H₁₈: C, 91.89; H, 8.11. Found: C, 91.09; H, 8.05.

The physical constants of this hydrocarbon and of the one obtained by the dehydration of *tert*.-butyldiphenylcarbinol are as follows.

TABLE I
PHYSICAL CONSTANTS

Compound	B. p., °C.	d_4^{20}	n_D^{20}	M_D	
				Calcd.	Obs.
Diphenyl-3,3-methyl-2-butene-1	132–133 at 4.5 mm.	1.0060	1.5757	73.05	73.03
C ₁₇ H ₁₈ from <i>tert</i> .-butyldiphenylcarbinol	125–128 at 3.5 mm.	1.0007	1.5730	...	73.08

A second fraction which boiled a little higher was collected. Its index of refraction was near that of the main fraction but analysis showed that it contained some oxygen.

The identification of the two hydrocarbons as samples of the same compound was completed by taking small samples of each in an absolute alcohol-ether solution and treating with dry hydrogen chloride. On standing the solid chloride separated and on recrystallization from alcohol and ether mixture it melted at 102–106° in each case. A mixed melting point showed no depression.

Ozonization of Diphenyl-3,3-methyl-2-butene-1.—A mixture of air and ozone was bubbled through a solution of 45 g. of the unsaturated hydrocarbon (obtained by the dehydration of diphenyl-*tert*.-butylcarbinol) in 200 cc. of glacial acetic acid for four

hours.¹⁰ More acetic acid was added from time to time to replace that lost by evaporation. The solution was then treated with water and the acetic acid neutralized with 20% sodium hydroxide solution. The ketone was collected in ether, the ether solution dried over sodium sulfate, filtered and evaporated. The ketone was distilled under reduced pressure. The yield was 32 g. of a yellow oil; b. p. 132–135° at 2 mm.; d_4^{20} 1.069; n_D^{20} 1.5748; M_D , calcd., 68.91; found, 69.21. This compound is described¹¹ as a solid melting at 41–41.5° and boiling at 310–311°. Our product did not solidify on standing for several days. It was analyzed as a check on its purity.

Anal. Subs., 0.2139: CO_2 , 0.6703; H_2O , 0.1382. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.51; H, 7.23.

Oxidation of Diphenyl-3,3-butanone-2 to Diphenylmethylacetic Acid.—In a 500 cc. round-bottomed flask, fitted with a mechanical stirrer, was placed a solution of 16.5 g. of sodium hydroxide in 140 cc. of water. The solution was cooled to 0° in an ice-salt bath and to the well-stirred solution was added 24 g. of bromine. The temperature was held at 0° during this addition. To the cold solution 11.4 g. of diphenyl-3,3-butanone-2 was added and the mixture was cooled and stirred for about three hours and then allowed to come to room temperature and stirred for another three hours. The flask was fitted with a condenser for distillation and the solution was distilled as long as bromoform came over with the water. It was necessary to add water to the reaction mixture from time to time. When the hydrolysis was complete, the alkaline reaction mixture was extracted with ether to remove unoxidized ketone and then acidified with dilute sulfuric acid. The acid which precipitated was filtered and recrystallized from 95% alcohol. It then melted at 173–174° and when mixed with a sample of diphenylmethylacetic acid prepared from diphenylmethylacetaldehyde showed no depression in the melting point.

Attempts to Prepare Di-*tert.*-butyltetraphenylethane. *Tert.*-butyldiphenylmethyl chloride was shaken with molecular silver in anhydrous toluene for long periods but the only product that could be isolated was the unsaturated hydrocarbon described above. It was also treated with magnesium in ether and then with cupric chloride. A brisk reaction occurred with magnesium but the unsaturated hydrocarbon was the only product that was isolated. The carbinol gave a deep red color with sulfuric acid but attempts to reduce the compound with vanadous chloride were unsuccessful.

Summary

1. The hydrocarbon $C_{17}H_{18}$ obtained by the dehydration of *tert.*-butyldiphenylcarbinol has been identified as diphenyl-3,3-methyl-2-butene-1.

URBANA, ILLINOIS

¹⁰ The procedure described by Noller with Adams, *THIS JOURNAL*, **48**, 1076 (1926) was followed.

¹¹ Thörner and Zincke, *Ber.*, **11**, 1989 (1878).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPPSALA]

THE APPLICATION OF THE OIL TURBINE TYPE OF ULTRACENTRIFUGE TO THE STUDY OF THE STABILITY REGION OF CARBON MONOXIDE-HEMOGLOBIN

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Depending on the experimental conditions, there are two principles by which molecular weights may be determined by means of the ultracentrifuge: the establishment of a sedimentation equilibrium between centrifuging and diffusion, and the measurement of the sedimentation velocity.² The first requires only a moderate centrifugal force of about 5000 times that of gravity but a relatively long time, generally two days. Unstable substances, for example, acid hemoglobin near the region of hematin formation, may be altered appreciably during this length of time. The second principle, on the other hand, requires for molecules of the order of magnitude of the proteins, centrifugal forces of at least 70,000 times that of gravity, introducing certain experimental difficulties, but enabling measurements to be made in as short a period as two hours of centrifuging, if necessary.

Although the sedimentation equilibrium method is sounder thermodynamically, the other method has certain advantages which justified the construction of an oil turbine type of ultracentrifuge capable of running at a speed of 42,000 r.p.m. and giving an effect 104,000 times that of gravity. In addition to the much smaller chance for decomposition of an unstable substance in the short time of centrifuging, it is possible to obtain more exact information when a mixture of molecules is present in a solution, whereas in the sedimentation equilibrium method only the resultant effect of centrifuging and diffusion is obtained; by using higher speed we determine the diffusion and the velocity of sedimentation separately. Under these conditions it is possible to detect anomalies in the diffusion produced by labile gel formation or hydration that might otherwise cancel out or be disguised.

Previous communications³ have given results obtained through the use of the sedimentation equilibrium method on hemoglobin and egg albumin. The present paper will give a short description of the high-speed oil turbine type of ultracentrifuge and determinations on the range of P_H over which hemoglobin can exist in its normal form.

¹ Fellow of the International Education Board.

² The Svedberg, *Kolloid-Z.*, 36, 57, 60 (1925).

³ (a) Svedberg and Fåhræus, *THIS JOURNAL*, 48, 430 (1926); (b) Svedberg and Nichols, *ibid.*, 48, 308 (1926).

Theory of the Sedimentation Velocity Method

After the very short initial period the centrifugal force per mole, $M(1-\rho V)\omega^2 x$, becomes equal but is of opposite sign to the frictional force, $f(dx/dt)$, where for dilute solutions $f = (RT/D)$. These quantities have their usual significance; M , the molecular weight; ρ , the density of the solution; V , the partial specific volume; ω , the angular velocity; x , the distance from the axis of rotation of the centrifuge; f , the frictional coefficient; t , the time; T , the absolute temperature; and D , the diffusion constant.

The expression for the molecular weight is, then, for small x -intervals,

$$M = \frac{RT}{D(1-V\rho)} \cdot \frac{dx}{\omega^2 x} = \frac{RTs}{D(1-V\rho)} \quad (1)$$

where $(1/\omega^2 x) \cdot (dx/dt) = s$ is the specific sedimentation velocity, a characteristic constant for every molecular species at a given temperature and for a given solvent. For large x -intervals it is necessary, of course, to use the integrated form of equation (1):

$$M = \frac{RT \ln \left(\frac{x_2}{x_1} \right)}{D(1-V\rho)\omega^2(h_2 - h_1)} \quad (2)$$

With a sufficiently strong centrifugal field of force it would be possible to measure directly the movement of the boundary of the dissolved substance with time, but generally sufficient diffusion occurs so that the boundary becomes too blurred to read off the x -values accurately. The boundary will become especially diffuse if there are several molecular species present of not very different weights. However, if sedimentation occurs rapidly enough so that pure solvent appears at the inner end of the solution column in a time short compared to the total time of centrifuging and if there is still a region of solution where there is no change of concentration with distance, then the true position of the boundary can easily be located. The theory of diffusion tells us that the place where the boundary would have been if there had been no diffusion is the surface where the concentration is half that of the original concentration of the solution. After a certain time of centrifuging, the constant part does not correspond to the original concentration in a sectorial cell, due partly to the fact that the molecules are thrown out radially and partly to the increased acceleration with distance. The gradual decrease in concentration with time can be calculated from the relation⁴

$$c_0 \left(\frac{x_0}{x_t} \right)^2, \quad (3)$$

c_0 being the original concentration and c_t the concentration at time t .

The diffusion constant can be determined independently of the centri-

⁴ Svedberg and Rinde, *THIS JOURNAL*, **46**, 2684 (1924).

fuging, if desired, but it is more reliable to calculate it under the same conditions from the same observations used to determine the sedimentation velocity. When pure solvent is obtained above the solution in a time short with respect to the total time, then the diffusion constant may be conveniently determined from the simple diffusion equations

$$c_s = \frac{c_0}{2} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy \right) \quad \left| \quad y = \frac{z}{\sqrt{4Dt}} \right. \quad (4)$$

in which c_s is the concentration at the distance z from the meniscus after the time t ; c_0 , the concentration of the unchanged part of the solution; and $\frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy$, the probability integral.

If a sufficiently high field of force is not available, then the more involved expression^b must be used

$$\frac{c_x}{c_0} = -\frac{B\sqrt{t}}{\sqrt{D\pi}} e^{-\frac{(Bt-x)^2}{4Dt}} + \frac{1}{2} \left[1 - \Theta \left(\frac{Bt-x}{\sqrt{4Dt}} \right) \right] + \frac{1}{2} e^{\frac{Bx}{D}} \left[1 + \frac{B}{D} (Bt+x) \right] \left[1 - \Theta \left(\frac{Bt+x}{\sqrt{4Dt}} \right) \right] \quad (5)$$

where B is the sedimentation velocity and $\Theta \left(\frac{Bt-x}{\sqrt{4Dt}} \right)$ and $\Theta \left(\frac{Bt+x}{\sqrt{4Dt}} \right)$ are probability integrals with the arguments indicated. Since this equation was derived for a gravitational field, it should be used only for very small x -intervals in a centrifugal field. Furthermore, there must be a region of constant concentration so that the liquid may be regarded as unlimited in the direction of the periphery.

With a centrifugal field 70,000 times that of gravity it is permissible to use the simple equations (4) after four hours of centrifuging for a substance of molecular weight 16,700 and after two hours for a weight of 33,400.

Apparatus and Method

The apparatus developed⁶ may be conveniently divided into the centrifuge proper,⁷ the oil circulation system, the vacuum and hydrogen system, the optical system and the stroboscopic tachometer.

The most important conditions which the centrifuge had to fulfil were: a centrifugal force in the cells of 80,000–100,000 times the force of gravity,

^b Mason and Weaver, *Phys. Rev.* [2] 23, 424 (1924).

⁶ For a complete description of the apparatus see Svedberg and Lysholm, *Nova Acta Reg. Soc. Scient. Upsaliensis*, Vol. ex. ord., ed. 1927.

⁷ The centrifuge proper was built in the workshops of Ljungström Steam Turbine Company through the courtesy of Mr. F. Ljungström, who suggested the use of high pressure oil turbines for driving the centrifuge. Most of the other parts of the apparatus were made in the workshops of this Laboratory. Mr. A. Lysholm, chief engineer, should be credited as the designer of the centrifuge.

temperature in the cells not higher than 35° , amplitude of vibration small enough so that sharp photographs could be taken during centrifuging at high speed, optical parts inside the centrifuge remaining free from oil dust. Fig. 1 shows the rotor, cylindrical in shape, 150 mm. in diameter, and 60

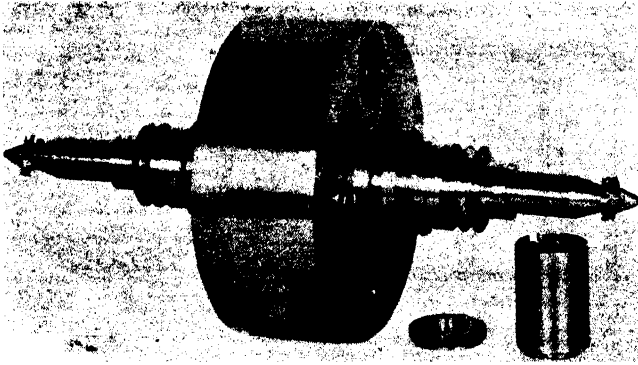


Fig. 1.

mm. thick. It is made of chrome nickel steel and has openings for four cells. It is driven by high pressure oil impinging against two eight-bladed oil turbines, one at each end of the shaft. The turbines receive 240

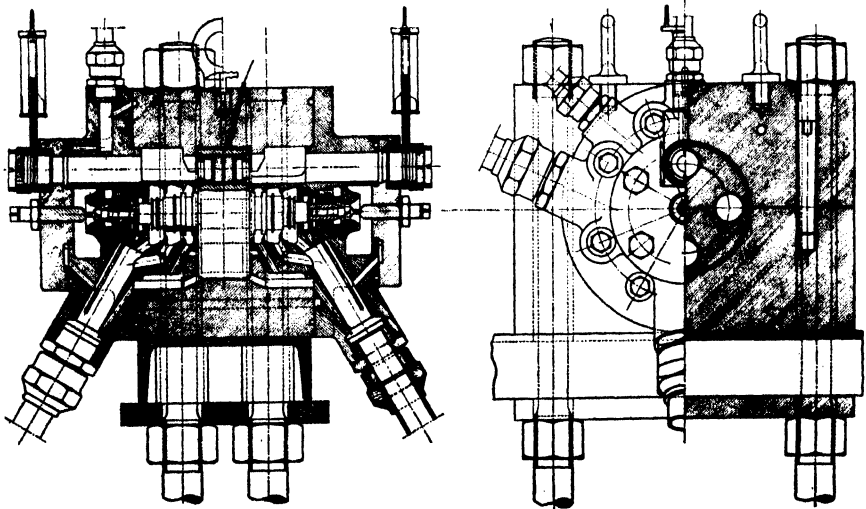
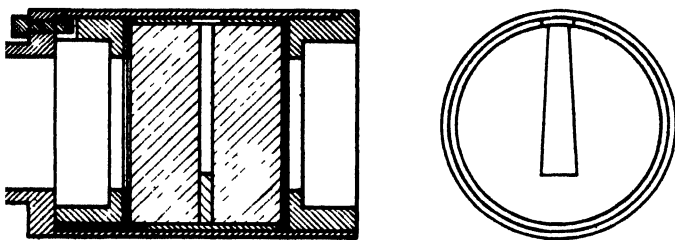


Fig. 2.

liters of oil per minute, and at the same time 7 liters of oil per minute lubricate and cool the bearings. The rotor revolves in hydrogen gas at a reduced pressure to avoid undesirable heat production in the rotor chamber.

The oil from the bearings is prevented from entering the rotor chamber by an elaborate system of oil rings and oil deflectors.

The centrifuge is shown diagrammatically in Fig. 2. To the left is an axial section, and to the right a section at right angles to the axis of rotation. The chief parts are the rotor, top and bottom casings, and the two end brackets. The top casing has the hydrogen inlet and carries the thermocouple for the measurement of the temperature of the



interior of the centrifuge. The end brackets contain the turbine chambers with inlets and outlets for the oil that has been pressed through the bearings. The main bearings and the plates for the pivot thrust bearings of the shaft are here also. Thermocouples are inserted into the bearings to ascertain their temperatures. An observation channel 34 mm. in diameter is bored through the end brackets and top casing and closed by round glass or quartz windows 10 mm. thick, protected from oil dust by special electromagnetically operated shutters.

The cells for the solution to be studied are made as follows. Two round glass or quartz plates 30 mm. in diameter and 10 mm. thick are cemented with a de Khotinsky cement having a high softening temperature to a third plate 30 mm. in diameter and 1.90 mm. thick. The latter has a sectorial aperture of 5°. The cell is cemented to a steel collar (a brass collar becomes deformed in time) having an opening coincident with the opening of the sectorial cell. This collar containing the cell

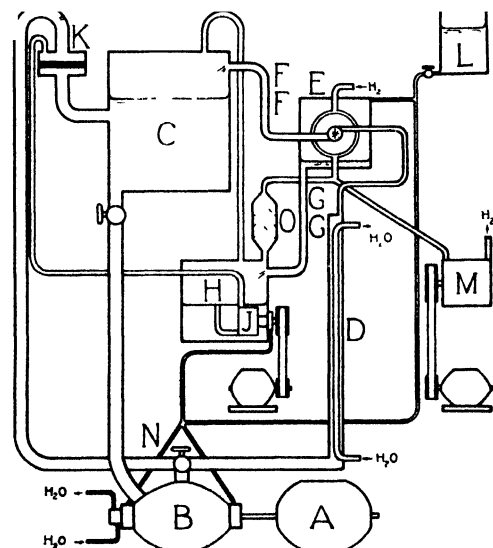


Fig. 4.

is then put into a steel shell (shown in Fig. 1) and supported at both ends by a system of sectorial disks and diaphragms (Fig. 3) so that actually a 3° sectorial cell is used. The steel shell bearing the cell is held in place in the rotor by means of a guard ring.

Fig. 4 shows the oil circulation system. The centrifugal pump B, driven by the

20 H. P. three-phase motor A, sucks the oil⁸ from the container C and forces it through the oil cooler D to the centrifuge E. From the turbine the oil passes through the pipes FF (only one is shown in the diagram) and back to the container. The oil pumped through the bearings drains down to the lower container H through the pipes GG. A small pump J then raises it again to the upper container C, forcing it through the filter K on its way. Before starting a run the whole oil flow is directed through the filter by means of the three-way valve N in order to remove suspended material which would wear away the bearings too rapidly. M is the vacuum pump, L the container for the oil employed for keeping the various joints vacuum-tight and O is a trap for oil droplets. Speed regulation of the centrifuge is obtained through changing the oil pressure by varying the speed of the main oil pump motor. In Fig. 5 is given the relation between oil pressure and speed of the centrifuge.

In hydrogen as well as in air at atmospheric pressure the rotor warmed up more than 10° above room temperature in a few minutes. Even a 0.5 mm. air vacuum obtained by the oil vacuum pump (M, Fig. 4) did not prevent injurious heating because the heat generated in the residual air cannot be conducted away rapidly enough. However, the heat conductivity of hydrogen is high and independent of pressure down to about 20 mm. of Hg, below which the conductivity decreases.⁹ But heat production decreases continuously with decreasing pressure and would become negligible at very small hydrogen pressures (as indicated by the dotted line, Fig. 6) if its dissipation were not radically hindered by the rapid decrease in heat conductivity of air below a pressure of 1 mm. of Hg and of hydrogen below 20 mm. of Hg. Therefore there must be an optimum pressure of hydrogen which will give the smallest temperature difference. The most favorable hydrogen pressure was found to be 12–15 mm. of Hg, as indicated by Fig. 6, where the ordinates give the temperature differences found to exist between the rotor and the casing of the centrifuge for different pressures of hydrogen. Therefore, hydrogen is let in from a container of compressed gas at a rate sufficient to maintain a pressure of 15 mm. of Hg while the vacuum pump keeps the system air-free during the centrifuging.

Resistance thermometers are used to ascertain the temperatures of the incoming and outgoing water of the oil cooler, the incoming and outgoing oil, the oil container and the cold junction of the thermocouples. Thermo-

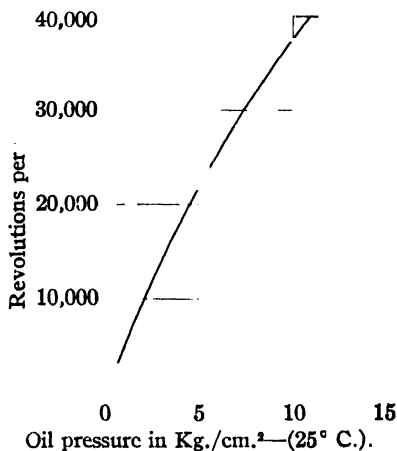


Fig. 5.

⁸ Gargoyle Velocite Oil E is most suitable because of its low vapor pressure and low viscosity.

⁹ Soddy and Berry, *Proc. Roy. Soc. (London)*, **84A**, 582 (1911).

couples give the temperature of the main bearings and the top casing of the centrifuge. To determine the difference in temperature between the rotor and the top casing a substance or mixture of known melting point was put into the cell and subjected to the same experimental conditions as in the experiment. Azoxybenzol and piperonal mixtures give a temperature region in the vicinity of 30° . If a thin layer of substance is used the pressure effect on the melting point is negligible. The temperature difference was found to be 1.4° , ordinarily, with a hydrogen pressure of 12–15 mm. of Hg, so the temperature of the cell is then determined by adding this value to the reading of the top casing thermocouple.

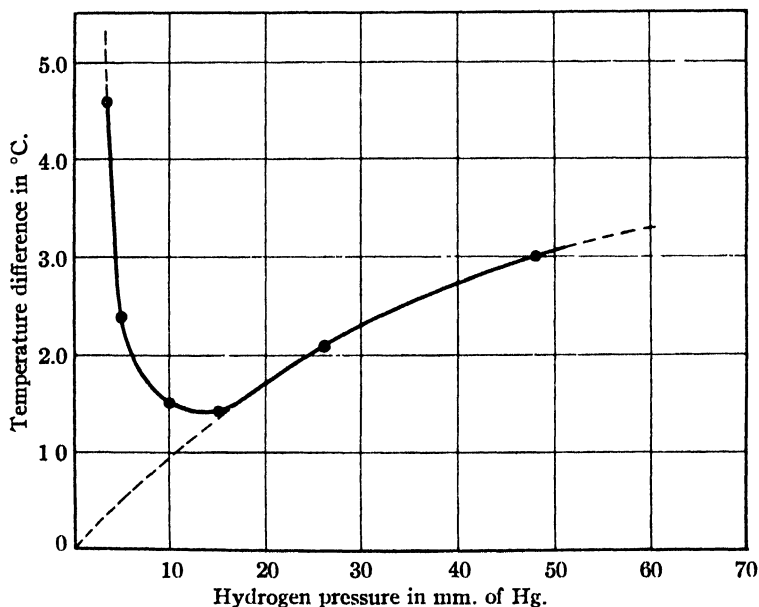


Fig. 6.

The optical system is shown in Fig. 7. Parallel light is produced by focusing the image of the incandescent ball of the fixed-focus 100 c. p. "Pointolite" lamp B on the diaphragm D by means of a Dallmeyer lens C_1 of aperture $f:1.9$ and focal length 7.5 cm. The light from the diaphragm is then made parallel by means of a Zeiss-Tessar lens C_2 , of aperture $f:4.5$ and focal length 15 cm. E_1 and E_2 are a water filter and a light filter, respectively. For the visible and the long-waved ultraviolet region of the spectrum a special Zeiss anastigmatic lens H of aperture $f:12.5$ and focal length 99 cm. was used. G is the camera.

Since the rotor should run free of any gearing arrangement, the speed of the centrifuge is determined by a stroboscopic tachometer. At the back of the camera a motor J is mounted (Fig. 7) carrying a perforated disk K. The stroboscope motor is connected to a small generator M, which acts on a hot-wire ammeter calibrated to read revolutions per minute directly. To measure the speed, the rotating cell is observed through the holes of the revolving disk of the stroboscope and the speed of the motor adjusted by

means of the resistance L until the cell appears to come to a stop, at which time the speed is read off from N .

The rotor must be balanced to within a few centigrams, otherwise injurious vibration will occur. A balancing machine similar to the Lawaczeck-Heymann apparatus¹⁰ is quite suitable. The rotor is supported by two horizontal V-bearings lined with Babbitt metal. The bearings are fixed on top of two stiff vertical steel springs, one of which carries a small mirror for reflecting the image of a straight filament lamp onto a scale. By means of a small motor the rotor is given a speed corresponding to a vibration period above the resonance value of the springs. The rotor is then allowed to run free, and as its speed decreases through the resonance point the amplitude of vibration is read off on the scale. By systematic trial of small lead pieces put into the steel shells the unbalance can be reduced to a few milligrams.

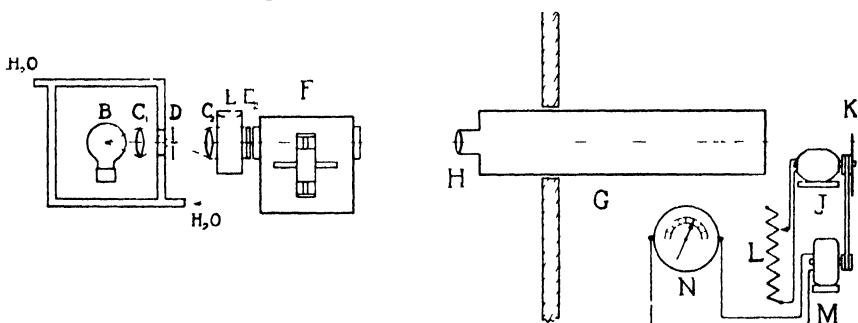


Fig. 7.

The general procedure for carrying out an experiment is as follows. One cell is filled with the solution to be studied and another with a standard for comparison of light intensities (potassium chromate is satisfactory for the whole range blue-short ultraviolet of the spectrum). Then vacuum oil is added to form a layer 2 mm. thick on top of the solutions to prevent boiling caused by the hydrogen vacuum in the rotor chamber and to prevent the rise of convection currents. At a speed of 10,000 r.p.m. the 2 mm. of oil in the cells exerts a pressure of one atmosphere; therefore, since the vacuum pump is not started until an oil pressure of 3 kg./cm.² is reached, corresponding to a speed of 14,000 r.p.m., the solution is protected the whole time.

The cells in their steel shells are inserted into the rotor and the contact surfaces of the top casing are rubbed with wool fat to make the centrifuge vacuum-tight. Then the lid is put on and screwed tight and the windows with their electromagnetic shutters are put in place at the ends of the observation channel of the centrifuge.

¹⁰ Heymann, *Elektrotech. Z.*, 40, 235 (1919).

After removing air bubbles from the centrifugal oil pump the big motor is gradually set in motion and the vacuum pump started when a pressure of 3 kg./cm.² is reached. The pump for the lower oil container is also started at this time. As soon as an air vacuum of 5 mm. of Hg is reached, hydrogen is admitted to the rotor chamber and the flow regulated at 1.0–1.5 kg./cm.² pressure to give a total pressure of 15 mm. of Hg in the centrifuge. The oil pressure is now increased until the desired speed is attained, regulating at the same time the water to the oil cooler to keep the oil entering the turbines at a temperature of 25°.

During the centrifuging, photographs of double natural size are taken at 30-minute intervals. After three hours a substance of molecular weight approximately 68,000 has centrifuged so completely at a speed of 40,000 r.p.m. that there is no longer a region of constant concentration in a column of solution 1.2 cm. in length. After stopping the centrifuge, a series of different concentrations of the same solution are pipetted into the cell and photographed on the same plate, the centrifuge being run at a low speed for this purpose. The plate after development is microphotometered and treated as previously described in the sedimentation equilibrium determinations.

Temperature and the speed of the rotor are measured from time to time during centrifuging, partial specific volume is determined pycnometrically and the diffusion constant either independently or from the photographs of the solution during centrifuging. It is better, however, to determine the diffusion constant from the centrifuging because its value may be decreased by the pressure developed at the high centrifugal forces used (about 10 atmospheres per millimeter of solution at a speed of 42,000 r.p.m.).

Experimental Part

Adair¹¹ found by osmotic measurements that hemoglobin, over a considerable range of hydrogen-ion concentrations (P_H 6.8–8.3), gives a normal osmotic pressure corresponding to a molecular weight of about 68,000, after correcting for the pressure of diffusible ions. However, the ultracentrifuge offers a means of determining the molecular weight directly, eliminating any correction for the presence of diffusible ions, provided a sufficient concentration of electrolyte is present to repress the Donnan effect.¹² A series of determinations was therefore made to verify and extend Adair's results.

Carbon monoxide-hemoglobin was prepared in the following manner. Horse blood was defibrinated by shaking for fifteen minutes with Jena glass pearls, saturated with carbon monoxide, and cooled to 0°. The corpuscles were separated from the serum by centrifuging and then washed five times with 1% sodium chloride. The concentrated mass of corpuscles was then dialyzed at 0° to hemolyze and yield crystals and a

¹¹ Adair, *Skand. Arch. Physiol.*, **49**, 76 (1926).

¹² Tiselius, *Z. physik. Chem.*, **124**, 458 (1926).

saturated stock solution. Since the stroma cannot be centrifuged off from a concentrated solution of hemoglobin, they were removed by a method suggested by A. Tiselius of this Laboratory and based on an observation by Heidelberger.¹³ According to the latter, a toluene layer over a solution of hemoglobin containing stroma soon acquires some swelled stroma due to the action of the toluene on the cholesterol of the stroma. The contents of the bags were shaken with toluene in a shaking machine for one hour at 0° and then centrifuged, yielding a thick jelly of swelled stroma which could be skimmed off. Complete removal of the stroma was effected in two shakings with toluene. Then an equal quantity of 0.2 *M* disodium phosphate was added to complete the solution of the crystals and sufficient molar potassium dihydrogen phosphate added to bring the hemoglobin to its isoelectric point, *P_H* 6.7, following a procedure similar to that of E. J. Cohn.

The solution at this point still contains globulins, so further purification is necessary. Saturated ammonium sulfate solution was added slowly until crystals of hemoglobin just started to form, as indicated by the streaming effect of the small plate-like crystals in motion. This occurs when the solution becomes about 15% saturated with ammonium sulfate. Crystallization was allowed to continue for three days and then the crystals were centrifuged off and dialyzed to remove the ammonium sulfate, yielding an 11% solution of pure hemoglobin with a mass of crystals at the bottom of the bags. The solution was resaturated with carbon monoxide and used exclusively for the centrifuging. The crystallization from 15% saturated ammonium sulfate solution is not complete, so after the first crop of crystals is removed more ammonium sulfate may be added to the mother liquor to cause the remaining hemoglobin to crystallize. This crop may be somewhat contaminated, so it should be dissolved again and recrystallized.

The partial specific volume of the hemoglobin was determined at 30° over the range of hydrogen-ion concentrations studied and found to increase gradually from 0.7545 at a *P_H* of 6.0 to a low maximum, 0.759, in the neighborhood of a *P_H* of 9 for dilute solutions.

All of the centrifuging experiments were performed on carbon monoxide-hemoglobin solutions of 0.95–1.0 g. per 100 cc. Parallel light with a Lifa blue filter was employed throughout. The determinations therefore refer to the light absorption of the hemoglobin absorption band at 410 μ . The usual time of exposure for Hauff Ultra Rapid plates was 20–40 seconds, and the plates were ordinarily developed three minutes in Ilford metol developer or two minutes in Eclipse metol-hydroquinone developer.

Three different buffers were used: Walpole's acetic acid-sodium acetate for solutions more acid than a *P_H* of 5.5, Sørensen's primary-secondary phosphate mixtures for the range *P_H* 5.8–7.7, and Ringer's secondary sodium phosphate-sodium hydroxide mixtures for solutions more alkaline than *P_H* 7.7.

Table I is typical of the results obtained for the sedimentation velocity from centrifuging. It refers to a solution of carbon monoxide-hemoglobin at a *P_H* of 7.56 in primary-secondary phosphate buffer 0.0191 *M* with respect to phosphate. Fig. 8 gives a reproduction of the photographic record of the centrifuging, showing the conditions of the solution 0.5 hr., 1 hr., etc., up to 3 hrs. after the start of the run. Immediately above the sedimentation record is the potassium chromate standard for adjusting the light intensity to the same value throughout. The top row is the scale of concentrations.

From the variation of concentration with distance from the center of rotation after 1, 1.5, 2, 2.5 and 3 hours the diffusion constant was cal-

¹³ Heidelberger, *J. Biol. Chem.*, 53, 32 (1922).

TABLE I

EXPERIMENT 56. SPECIFIC SEDIMENTATION VELOCITY OF CARBON MONOXIDE-HEMOGLOBIN, $P_H = 7.56$

Concentration 0.99 g. per 100 cc.; primary-secondary phosphate buffer, 0.0191 M phosphate; $V = 0.7575$ at 30° ; $\rho = 1.0005$; $T = 303.1^\circ$; length of column = 1.17 cm.; thickness of column = 0.20; Hauff Ultra Rapid plates, Lifa blue filter; exposure time = 30 sec.; Ilford metol developer, $2\frac{1}{4}$ min.

Time interval, hours	Δx per 0.5 hr.	x med., cm.	Speed, r.p.m.	Centrif. force, $\omega^2 r$	Spec. sediment, velocity, s in cm./sec.
0.5-1.0	0.080	4.911	38,700	8.066×10^7	5.46×10^{-13}
1.0-1.5	.080	4.990	38,820	8.246×10^7	5.36×10^{-13}
1.5-2.0	.085	5.072	38,750	8.353×10^7	5.58×10^{-13}
2.0-2.5	.086	5.158	38,700	8.471×10^7	5.48×10^{-13}
2.5-3.0	.087	5.244	38,720	8.622×10^7	5.44×10^{-13}

Av. 5.46×10^{-13}

culated, giving a mean value of $0.0736 \text{ cm.}^2/\text{day}$ at 30° . Using equation (1), the above data then give a mean molecular weight of 66,800.

8/8 7/8 6/8 5/8 4/8 3/8 2/8 1/8 0/8



Concentration scale.

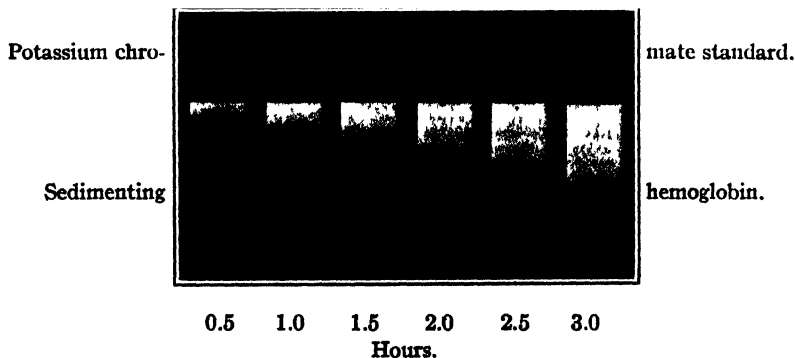


Fig. 8.

Fig. 9 gives the variation of concentration with distance after 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours of centrifuging of the same hemoglobin solution. These curves have been corrected by means of formula (3) for the gradual decrease in concentration of the solution with time due to the sector-shaped cell and the increase in acceleration with distance from the center of rotation. The dotted curves for 2 and 3 hours represent the theoretical diffusion curves of a substance of only one molecular species if subjected to the same experimental conditions. The agreement is evidently extremely

good, and since the small deviations at the ends of the curves cancel one another in the curves for 2 and 3 hours they are probably purely accidental.

Table II gives the results obtained over the P_H range 5.4 to 10.2. In many cases the values of the diffusion constant and sedimentation velocity were determined for each experiment from two plates taken with different times of exposure. The acetate buffer used for the P_H 5.4 was 0.091 M with respect to acetate. The double phosphate buffer for the two experiments at P_H 6.0 and for the two at P_H 7.56 was 0.0191 M , but for P_H

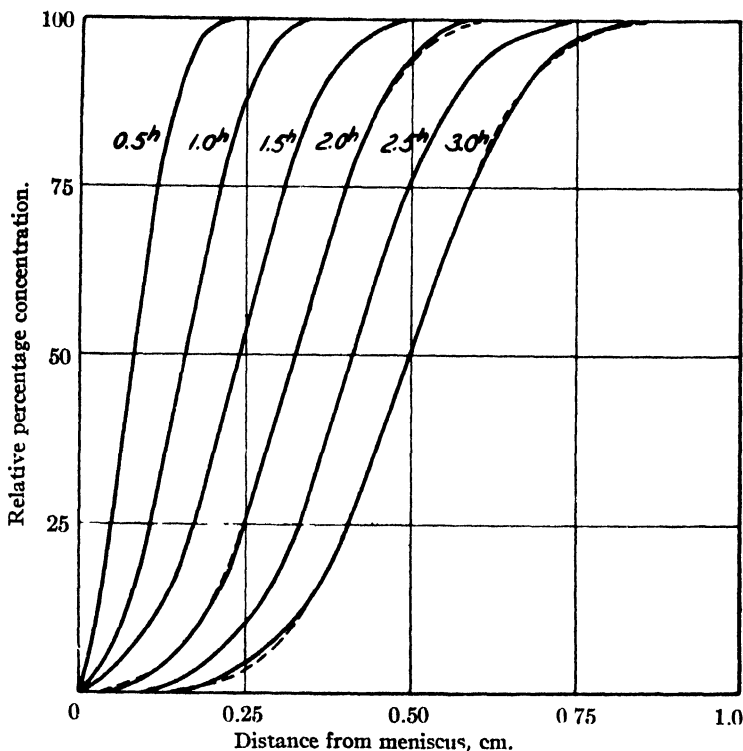


Fig. 9.

6.5 it was 0.06 M with respect to phosphate. The secondary sodium phosphate-sodium hydroxide buffer for the two experiments at P_H 9.05 was 0.0191 M , but for P_H 10.2 it was 0.091 M with respect to phosphate. The length of the column of solution was 11–12 mm. for all runs except No. 54 and D, for which it was 13.7 and 15.5 mm., respectively. Experiment D refers to a dialyzed solution, salt-free.

It will be seen from the table that carbon monoxide-hemoglobin exists as molecules of weight 68,000 over the whole range of P_H 6.0 to 9.05, but that below P_H 6.0 and above P_H 9.05 some change has occurred, as indicated by the low sedimentation velocity and high relative diffusion

TABLE II

INFLUENCE OF P_H ON THE DIFFUSION CONSTANT, SEDIMENTATION VELOCITY AND MOLECULAR WEIGHT OF CARBON MONOXIDE-HEMOGLOBIN

Expt.	P_H	Speed, r.p.m.	Mean cen- trifugal force	Partial specific volume, V	D cm. ² /day	M	Spec. sediment. velocity, s in cm./sec.
66	5.40	41,800	9.90×10^7	0.7545	0.085	4.58×10^{-13}
58	6.0	38,700	8.32×10^7		.073	66,700	5.49×10^{-13}
				0.7545	.069	70,110	5.47×10^{-13}
59	6.0	38,500	8.32×10^7		.070	70,650	5.48×10^{-13}
54	6.5	38,900	8.09×10^7				
				0.755			
D	6.6	39,300	7.95×10^7		.070	68,340	5.41×10^{-13}
56	7.56	38,700	8.35×10^7		.074	66,800	5.46×10^{-13}
				0.7575			
57	7.56	38,900	8.45×10^7		.071	68,650	5.43×10^{-13}
61	9.05	41,500	9.72×10^7		.0655	69,210	5.00×10^{-13}
				0.759			
68	9.05	42,400	10.29×10^7		.0636	70,500	4.93×10^{-13}
67	10.2	41,200	9.59×10^7	0.7575	.070	4.48×10^{-13}

constant. The diffusion constant for P_H 10.2 has a fairly low absolute value on account of the hydration of the molecule which will be mentioned below. This change may be only apparent and in reality be caused by a small Donnan effect still unrepressed, or it may be due to a splitting up of the molecules. Sufficient data have not been accumulated as yet to decide between these possibilities because qualitatively these two phenomena act similarly on the diffusion constant and the sedimentation velocity of an ionized particle.

Experiments 61 and 68 very clearly show a hydration effect. For both runs a low sedimentation velocity and an equally low diffusion constant were obtained, giving an average of 0.91 of the normal values $D = 0.071$ cm.²/day and $s = 5.46 \times 10^{-13}$ cm./sec. Table III shows in more detail the effect of hydration on the centrifuging.

TABLE III

EXPERIMENT 61. CARBON MONOXIDE-HEMOGLOBIN AT P_H 9.05

Concentration, 0.99 g. per 100 cc.; secondary phosphate-sodium hydroxide buffer, 0.0191 M phosphate; $V = 0.759$ at 30° ; $\rho = 1.0007$; $T = 303.1^\circ$; length of column = 1.17 cm.; exposure time, 20 sec.; 3 min. development in half-strength Eclipse metol-hydroquinone developer.

Time int., hours	Δs per 0.5 hr.	s med. in cm.	Speed, r.p.m.	Centrif. force, $\omega^2 r$	D cm. ² /day	M	cm. ² /sec.
1.0-1.5	0.086	4.9950	41,230	9.31×10^7	0.0654	68,430	4.94×10^{-13}
1.5-2.0	.090	5.0830	41,570	9.65×10^7	.0649	69,300	4.97×10^{-13}
2.0-2.5	.091	5.1735	41,400	9.72×10^7	.0639	70,400	4.96×10^{-13}
2.5-3.0	.094	5.2660	41,530	9.96×10^7	.0669	67,550	4.99×10^{-13}
2.5-3.03	.102	5.2700	41,530	9.97×10^7	.0635	70,900	5.06×10^{-13}
					.0649	Av.	4.98×10^{-13}

The diffusion constant and the specific sedimentation velocity should be reduced in exactly the same ratio if hydration is present. This can easily be shown from the following considerations.

If we assume the water molecules attached to the hemoglobin to have their normal density, the centrifugal force on the hydrated particle will remain unchanged but the opposing viscous force will be increased. Calling the radius of the hemoglobin molecule r and that of the hydrated molecule R_1 , then

$$\frac{4}{3} \pi r^3 (\rho_{\text{Hb}} - \rho_d) \omega^2 x = 6\pi\eta R_1 \frac{dx}{dt}$$

where $(\rho_{\text{Hb}} - \rho_d)$ is the difference in density of the hemoglobin molecule from that of the dispersion medium. Rearranging

$$\frac{2}{9} \frac{(\rho_{\text{Hb}} - \rho_d)}{\eta} \cdot \frac{r^3}{R_1} = \frac{1}{\omega^2 x} \cdot \frac{dx}{dt} = S_{\text{obs.}}$$

$$S_{\text{obs.}} = \frac{r}{R_1} \cdot s$$

where $S_{\text{obs.}}$ and s are, respectively, the observed and the normal specific sedimentation velocities.

Likewise $D_{\text{obs.}} = (RT/6\pi\eta R_1) = (r/R_1) \cdot D$, where $D_{\text{obs.}}$ and D are the observed and the normal diffusion constants, respectively. Thus, both s and D should be reduced by the same ratio, (r/R_1) , if hydration has taken place; (r/R_1) was found to be 0.91 at a P_{H} of 9.05.

Now the number of water molecules held by a hemoglobin molecule can be calculated. Taking the density of a normal hemoglobin molecule as 1.33, the volume of a particle of molecular weight 66,800 is 82.9×10^{-21} cc. The volume of the hydrated particle is then 110.0×10^{-21} cc. and the volume of the water attached is 27.1×10^{-21} cc. The molecular volume of water at 30° is about 18.1 cc.; therefore the *free* volume of one molecule is 2.99×10^{-23} cc. The number of water molecules held by a hemoglobin molecule is then $27.1 \times 10^{-21} \div 2.99 \times 10^{-23} = 907$.

It is interesting to compare this value with the minimum number required to form a monomolecular layer on the hemoglobin molecule. The total surface of the Hb molecule considered as a sphere is 91.95×10^{-14} sq. cm. The cross section of a water molecule taken as a cube is 9.64×10^{-16} sq. cm. Therefore the minimum number that can be packed on the surface of a hemoglobin molecule is 954.

If the water molecules are considered as spheres the effective surface to be covered is that of a sphere of radius equal to the sum of the radii of the Hb and of the water molecules and is 105.7×10^{-14} . Assuming "cubical" packing the minimum possible number of water molecules is 713, but with hexagonal packing the number becomes 823. Hexagonal packing is the most probable mode of packing and since 823 is the *minimum* number possible, it is permissible to conclude that at a P_{H} of 9.05 there is a monomolecular layer of water surrounding the Hb molecules. A similar effect

of lesser magnitude was observed at a P_H of 7.73, using a low concentration of the secondary phosphate-sodium hydroxide buffer. But both solutions were poorly buffered, because the addition of the 1% protein changed the original P_H of the buffer by more than one P_H unit; therefore, since at P_H 7.56 a solution well buffered with primary-secondary buffer showed no hydration, this hydration effect is perhaps repressed if the solution is properly buffered. When more data have been collected this point can be decided.

The condition of the hemoglobin at the extremes of P_H and a fuller discussion of the phenomena occurring will be taken up in a later paper.

The rather high expenses connected with the construction of this centrifuge have been defrayed by grants from the foundation "Therese och Johan Anderssons Minne" and from the Nobel Fund for Chemistry.

Summary

1. An oil turbine type of ultracentrifuge has been described capable of running at a speed of 42,000 r.p.m. and yielding a centrifugal force 104,000 times that of gravity.

2. Determinations of the influence of P_H on the diffusion constant, molecular weight and specific sedimentation velocity of carbon monoxide-hemoglobin are reported over a P_H range 5.4–10.2. The diffusion constant and the specific sedimentation velocity are normal, respectively, 0.071 cm.²/day and 5.46×10^{-13} cm./sec. at 30° over the range of P_H 6.0–7.56, and the molecular weight is normal, 68,000, at least from a P_H of 6.0 to 9.05.

3. At a P_H of 9.05, in the neighborhood of a maximum in the partial specific volume curve, the Hb molecule appears to hold a monomolecular layer of water at its surface.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

VARIOUS ω -CYCLOHEXYLALKYL ALKYL ACETIC ACIDS AND THEIR ACTION TOWARD *B. LEPRAE*. VIII¹

BY ROGER ADAMS, W. M. STANLEY, S. G. FORD AND W. R. PETERSON²

RECEIVED AUGUST 29, 1927

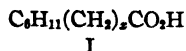
PUBLISHED NOVEMBER 5, 1927

In an earlier paper the ω -cyclohexyl derivatives of various normal aliphatic acids containing from one to thirteen carbon atoms in the side chain were described and their bactericidal character toward *B. Leprae*

¹ For previous articles in this field see (a) Shriner and Adams, *THIS JOURNAL*, **47**, 2727 (1925); (b) Noller with Adams, *ibid.*, **48**, 1074 (1926); (c) **48**, 1080 (1926); (d) Hiers with Adams, *ibid.*, **48**, 1089 (1926); (e) Van Dyke and Adams, *ibid.*, **48**, 2393 (1926); (f) Sacks with Adams, *ibid.*, **48**, 2395 (1926); (g) Hiers with Adams, *ibid.*, **48**, 2385 (1926).

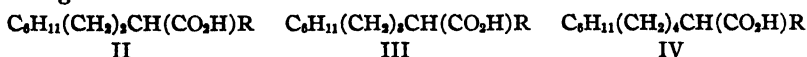
² This communication is an abstract of the theses submitted by W. M. Stanley, S. G. Ford and W. R. Peterson in partial fulfilment of the requirements for the degree *maîtrise* at the University of Illinois.

and other acid-fast was bacteria tested. The acid with the three-carbon side chain showed a very slight action, but with increase in the length of the side chain the bactericidal character increased until a maximum was reached in the molecule with a nine-carbon side chain (I)



This investigation had as its object the synthesis of acids isomeric with those previously studied, containing the cyclohexane ring with side chains of varying length but with the carboxyl in positions other than at the end of the chain. From bactericidal tests it could then be determined whether the position of the carboxyl group at the end of the chain as in the natural acids is important, or whether the chief function of the carboxyl may possibly be the solubilizing of the molecule. Moreover, the new acids, if bactericidal, would lead to further conclusions in regard to the significance of molecular weight either of the whole molecule or of the side chain.

In this communication three series of acids have been described: β -cyclohexylethyl alkyl (II), γ -cyclohexylpropyl alkyl (III), δ -cyclohexylbutyl (IV) alkyl acetic acids, and the alkyl group has been varied in series (II) from ethyl to *n*-octyl, in series (III) from ethyl to *n*-heptyl and in series (IV) from ethyl to *n*-hexyl. Three isomers of each acid containing in the side chain from eight to twelve carbon atoms and holding the carboxyl group on the third, fourth and fifth carbon atoms from the ring, were thus made available in addition to a number of acids of lower molecular weight.



These acids were tested against the same strain of *B. Leprae* as that used in the earlier work (Table I). In series (II) the compounds with the R group as ethyl or propyl showed only a slight action, but with the *n*-butyl group they killed in a dilution of 1:40,000. The action rapidly increased with the size of the molecule until the *n*-heptyl and *n*-octyl showed a bactericidal action in dilutions of 1:220,000 and 1:320,000, respectively, far greater than the sodium salts of chaulmoogric or hydnocarpic acids or of the mixed acids from the saponified natural oils now used in the treatment of leprosy or of the ω -cyclohexyl aliphatic acids with the carboxyl at the end of the chain. The same results were obtained in series (III) and series (IV), the bactericidal action increasing very rapidly with the size of the molecule and the compounds isomeric with those in series (II) giving approximately the same bactericidal effect in the same dilutions. It is obvious that the position of the carboxyl group is probably of secondary importance. The value of this fact cannot be underestimated, because all of the most effective acids described in this paper are easily prepared as compared with the effective ones in which the carboxyl group is at the

end of the side chain. Moreover, investigation of the effect of other groups in the molecule such as various types of rings, amino groups, halogens, double bonds, etc., is rendered much easier in acids of this type.

TABLE I
BACTERIOLOGICAL TESTS TO *B. Leprae*
—Dilutions of sodium salts—

	10,000	20,000	30,000	40,000	50,000	60,000	70,000	80,000	90,000	100,000	110,000	120,000	130,000	140,000	150,000	160,000	170,000	180,000	190,000	200,000	220,000	240,000	260,000	280,000	300,000	320,000	340,000	
Cyclohexylethyl alkyl acetic acids, $C_6H_{11}(CH_2)_2CH(COOH)R$. R =																												
C_2H_5	-	+	+	+	+	+	+	+	+	+																		
$n-C_3H_7$	-	+	+	+	+	+	+	+	+	+																		
$n-C_4H_9$	-	-	-	-	+	+	+	+	+	+																		
$n-C_5H_{11}$	-	-	-	-	+	+	+	+	+	+																		
$n-C_6H_{13}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+								
$n-C_7H_{15}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+
$n-C_8H_{17}^a$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+
C_6H_5	-	+	+	+	+	+	+	+	+	+																		
Cyclohexylpropyl alkyl acetic acids, $C_6H_{11}(CH_2)_3CH(COOH)R$. R =																												
C_2H_5	-	-	+	+	+	+	+	+	+	+																		
$n-C_3H_7$	-	-	+	+	+	+	+	+	+	+																		
$n-C_4H_9$	-	-	-	-	-	+	-	-	+	-	+																	
$n-C_5H_{11}$	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	+	+								
$n-C_6H_{13}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	+	+
$n-C_7H_{15}$	-	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	+	+
C_6H_5	-	+	+	+	+	+	+	+	+	+																		
Cyclohexylbutyl alkyl acetic acids, $C_6H_{11}(CH_2)_4CH(COOH)R$. R =																												
C_2H_5	-	-	-	-	-	-	-	-	-	-	-	-	+	+	-	+	-	-	-	-	-	+	+	+	+	-	-	-
$n-C_3H_7$	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
$n-C_4H_9$	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-
$n-C_5H_{11}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	-	-	-
$n-C_6H_{13}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	+	+	+
C_6H_5	-	-	-	-	-	+	+	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

^a Not tested in dilutions under 190,000.

A maximum bactericidal effect is not reached until a certain sized side chain is present, for example, one containing ten, eleven or twelve carbon atoms. It is probable, therefore, that in acids of this type molecular weight plays an important role, perhaps by producing the proper physical properties in the compounds tested. It still remains to determine whether the side chain must be straight or whether it may be forked.

The allyl derivatives in each series of acids studied appeared to have essentially the same effect as the propyl derivatives. Subcultures were made with many of the acids. Results showed that in all instances they were bactericidal and not merely inhibitive.

The three series of acids were prepared in one of two ways. The β -cyclohexylethyl bromide, γ -cyclohexylpropyl bromide and the δ -cyclohexylbutyl bromide were condensed with the sodium derivatives of diethyl alkyl malonates to give the corresponding diethyl- β -cyclohexylethyl, γ -cyclohexylpropyl or δ -cyclohexylbutyl alkyl malonates. The di-substituted malonic esters were saponified with alcoholic potassium hydroxide

and the dibasic acids decomposed in the usual way to give the monobasic acids. The second procedure merely consisted in introducing into the malonic ester the ω -cyclohexylalkyl group first and the alkyl group second. Apparently there is very little choice in the procedures.

Isomeric acids with the carboxyl on the first and second carbon atoms from the cyclohexane ring will soon be completed.

The bacteriological work was carried out by Gerald H. Coleman and W. M. Stanley.

Experimental

β -Cyclohexylethyl Bromide, γ -Cyclohexylpropyl Bromide and δ -Cyclohexylbutyl Bromide.—These alkyl halides were prepared according to the method described by Hiers with Adams.¹⁸

Alkyl Halides.—The alkyl halides were prepared from the corresponding alcohols. Of these alcohols, the *n*-amyl alcohol was produced from *n*-butyl magnesium bromide and formaldehyde,³ *n*-heptyl alcohol⁴ by the reduction of heptylic aldehyde with iron and acetic acid, *n*-octyl alcohol by the action of formaldehyde upon heptyl magnesium bromide,³ and *n*-nonyl alcohol⁴ either by the reduction of nonylic aldehyde with iron and acetic acid or by the condensation of *n*-heptyl magnesium bromide with ethylene oxide.¹⁸

Diethyl- ω -Cyclohexylalkyl Alkyl Malonates.—These were prepared by the condensation of ω -cyclohexylalkyl bromides with the sodium derivatives of diethyl alkyl malonates, using the usual procedure. The yields were quite satisfactory though they could be improved somewhat by distilling off the alcohol (in an oil-bath at 110–130°) from the sodium diethyl alkyl malonate before adding the ω -cyclohexylalkyl bromides and refluxing the mixture for several hours.

ω -Cyclohexylalkyl Alkyl Malonic Acids.—These acids were prepared by adding the diethyl- ω -cyclohexylalkyl alkyl malonates to an excess of hot, saturated alcoholic potassium hydroxide solution. The mixture was heated for an hour on a water-bath under reflux and then evaporated to dryness, taking particular care that all of the alcohol was removed. The solid potassium salt was dissolved in a little water and the dibasic acid precipitated with hydrochloric acid and extracted with ether. The malonic acids were purified by crystallization from benzene or acetone. If the former was used the product frequently contained benzene of crystallization. Where the dibasic acids were not

TABLE II

DIETHYL- β -CYCLOHEXYLETHYL ALKYL MALONATES, $C_6H_{11}(CH_2)_2C(CO_2C_2H_5)_2R$							
R =	B. p., °C.	n_D^{20}	d_4^{20}	$\overbrace{\text{Calcd., } \frac{\%}{H}}^C$		$\overbrace{\text{Found, } \frac{\%}{H}}^C$	
C_2H_5	146–148 (2 mm.)	1.4502	0.9907	68.30	10.13	68.39	10.04
$n-C_3H_7$	153–156 (6 mm.)	1.4518	.9813	69.16	10.32	69.45	10.14
$n-C_4H_9$	144–147 (4 mm.)	1.4531	.9714	69.88	10.50	69.56	10.39
$n-C_5H_{11}$	174–176 (5 mm.)	1.4537	.9644	70.52	10.66	70.36	10.61
$n-C_6H_{13}$	188–191 (5 mm.)	1.4539	.9569	71.12	10.81	71.31	10.42
$n-C_7H_{15}$	171–173 (3 mm.)	1.4545	.9527	71.67	10.94	71.71	10.93
$n-C_8H_{17}$	213–216 (7 mm.)	1.4550	.9449	72.19	11.07	71.94	10.89
C_8H_9	142–145 (2 mm.)	1.4563	.9915	69.62	9.74	69.54	9.66

³ For general procedure see "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1926, Vol. 6, p. 22.

⁴ *Ibid.*, p. 52.

readily handled they were decomposed directly to the monobasic acids without purification.

ω -Cyclohexylalkyl Alkyl Acetic Acids.—These were prepared by heating the malonic acids under reflux for two to three hours in an oil-bath at 20–30° above the melting point.

TABLE III

DIETHYL- γ -CYCLOHEXYLPROPYL, ALKYL MALONATES, $C_6H_{11}(CH_2)_3C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	$\begin{array}{c} \text{—Calcd., \%—} \\ \text{C} \quad \text{H} \end{array}$		$\begin{array}{c} \text{—Found, \%—} \\ \text{C} \quad \text{H} \end{array}$	
C_2H_5	149–151 (4 mm.)	1.4528	0.9797	69.17	10.33	69.01	10.43
$n\text{-}C_3H_7$	155–156 (4 mm.)	1.4531	.9743	69.87	10.51	69.81	10.53
$n\text{-}C_4H_9$	160–161 (4 mm.)	1.4534	.9620	70.53	10.66	70.46	10.70
$n\text{-}C_5H_{11}$	178–180 (4 mm.)	1.4549	.9603	71.13	10.81	71.05	10.72
$n\text{-}C_6H_{13}$	189–191 (4 mm.)	1.4551	.9501	71.68	10.95	71.71	10.98
$n\text{-}C_7H_{15}$	209–210 (5 mm.)	1.4554	.9471	72.18	11.07	71.74	11.18
C_8H_9	170–172 (5 mm.)	1.4569	.9837	70.30	9.94	70.10	9.88

TABLE IV

DIETHYL- δ -CYCLOHEXYLBUTYL, ALKYL MALONATES, $C_6H_{11}(CH_2)_4C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	$\begin{array}{c} \text{—Calcd., \%—} \\ \text{C} \quad \text{H} \end{array}$		$\begin{array}{c} \text{—Found, \%—} \\ \text{C} \quad \text{H} \end{array}$	
C_2H_5	165–167 (4 mm.)	1.4536	0.9704	69.87	10.50	69.61	10.24
$n\text{-}C_3H_7$	173–175 (4 mm.)	1.4538	.9695	70.52	10.66	70.59	10.43
$n\text{-}C_4H_9$	175–177 (4 mm.)	1.4546	.9563	71.12	10.81	71.02	10.44
$n\text{-}C_5H_{11}$	191–193 (5 mm.)	1.4559	.9530	71.67	10.92	71.43	10.79
$n\text{-}C_6H_{13}$	194–196 (4 mm.)	1.4572	.9514	72.19	11.07	72.40	10.86
C_8H_9	168–170 (4 mm.)	1.4565	.9742	70.94	10.13	70.83	10.09

TABLE V

β -CYCLOHEXYLETHYL, ALKYL MALONIC ACIDS, $C_6H_{11}(CH_2)_2C(CO_2H)_2R$

R =	M. p., °C.	Calcd., mol. wt.	Found, neut. equiv.
C_2H_5	114–115	242.2	243.6
$n\text{-}C_3H_7$	132–133	256.2	258.8
$n\text{-}C_4H_9$	135–136	270.2	269.1
$n\text{-}C_5H_{11}$	125–126	284.2	285.6
$n\text{-}C_6H_{13}$	108–109	326.3	328.4
C_8H_9	95–96	254.2	253.1

TABLE VI

γ -CYCLOHEXYLPROPYL, ALKYL MALONIC ACIDS, $C_6H_{11}(CH_2)_3C(CO_2H)_2R$

R =	M. p., °C.	Calcd., mol. wt.	Found, neut. equiv.
C_2H_5	143	256.2	254.8
$n\text{-}C_3H_7$	130	270.2	268.0
$n\text{-}C_4H_9$	138	284.2	281.1
$n\text{-}C_5H_{11}$	148	298.2	296.4
$n\text{-}C_6H_{13}$	134	312.2	312.4
$n\text{-}C_7H_{15}$	99	324.2	321.8

TABLE VII

 δ -CYCLOHEXYLBUTYL ALKYL MALONIC ACIDS, $C_6H_{11}(CH_2)_4C(CO_2H)_2R$

R =	M. p., °C.	Calcd., mol. wt.	Found, neut. equiv.
C_2H_5	136	270.2	271.6
$n-C_3H_7$	140	284.2	286.8
$n-C_4H_9$	113	298.2	301.6
$n-C_5H_{11}$	64	312.2	316.3
C_6H_5	143	282.2	284.1

TABLE VIII

 β -CYCLOHEXYLETHYL ALKYL ACETIC ACIDS, $C_6H_{11}(CH_2)_2CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calcd., mol. wt.	Found, neut. eq.	Calcd., C	% H	Found, C	% H
C_2H_5	121-124 (3 mm.)	1.4613	0.9619	198.2	199.0	72.66	11.19	72.52	11.41
$n-C_3H_7$	122-125 (2 mm.)	1.4623	.9486	212.2	213.2	73.51	11.41	73.42	11.46
$n-C_4H_9$	139-142 (4 mm.)	1.4624	.9410	226.2	228.0	74.22	11.58	74.02	11.43
$n-C_5H_{11}$	182-185 (5 mm.)	1.4626	.9350	240.2	242.9	74.93	11.74	75.14	11.76
$n-C_6H_{13}$	174-177 (2 mm.)	1.4628	.9283	254.2	258.0	75.53	11.89	75.21	11.66
$n-C_7H_{15}$	182-185 (2 mm.)	1.4631	.9222	268.3	266.0	76.04	12.02	75.73	11.86
$n-C_8H_{17}$	193-196 (4 mm.)	1.4640	.9193	282.3	281.8	76.51	12.14	76.86	11.89
C_6H_5	125-128 (2 mm.)	1.4672	.9714	210.2	208.0	74.22	10.55	74.16	11.44

TABLE IX

 γ -CYCLOHEXYLPROPYL ALKYL ACETIC ACIDS, $C_6H_{11}(CH_2)_3CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calcd., mol. wt.	Found, neut. eq.	Calcd., C	% H	Found, C	% H
C_2H_5	146-147 (3 mm.)	1.4622	0.9509	212.2	210.8	73.51	11.40	73.49	11.30
$n-C_3H_7$	148-150 (2 mm.)	1.4627	.9419	226.2	225.7	74.26	11.58	74.20	11.47
$n-C_4H_9$	153-154 (2 mm.)	1.4630	.9317	240.2	242.1	74.93	11.75	74.89	11.81
$n-C_5H_{11}$	188-192 (5 mm.)	1.4634	.9266	254.2	253.4	75.53	11.89	75.25	12.01
$n-C_6H_{13}$	208-211 (8 mm.)	1.4638	.9221	268.2	269.1	76.09	12.04	76.01	12.07
$n-C_7H_{15}$	199-203 (2 mm.)	1.4642	.9137	282.2	279.0	76.56	12.15	76.40	12.07
C_6H_5	147-150 (2 mm.)	1.4708	.9552	224.2	225.0	74.93	10.78	74.78	10.71

TABLE X

 δ -CYCLOHEXYLBUTYL ALKYL ACETIC ACIDS, $C_6H_{11}(CH_2)_4CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calcd., mol. wt.	Found, neut. eq.	Calcd., C	% H	Found, C	% H
C_2H_5	173-175 (3 mm.)	1.4622	0.9447	226.2	227.5	74.27	11.55	74.20	11.52
$n-C_3H_7$	156-158 (1 mm.)	1.4627	.9408	240.2	241.2	74.93	11.72	74.75	11.53
$n-C_4H_9$	178-180 (4 mm.)	1.4631	.9300	254.2	254.7	75.53	11.89	75.56	11.74
$n-C_5H_{11}$	207-209 (8 mm.)	1.4633	.9254	268.2	269.0	76.06	12.03	75.86	12.12
$n-C_6H_{13}$	187-189 (1 mm.)	1.4638	.9191	282.2	282.8	76.54	12.14	76.43	12.00
C_6H_5	174-176 (6 mm.)	1.4687	.9531	238.2	239.8	75.56	11.00	75.45	10.79

Summary

1. Three series of acids of the general formulas $C_6H_{11}(CH_2)_2CH(CO_2H)R$, $C_6H_{11}(CH_2)_3CH(CO_2H)R$ and $C_6H_{11}(CH_2)_4CH(CO_2H)R$ were prepared in which the R group was varied so that isomeric acids containing eight to twelve carbons, inclusive, in the side chain were produced. Some acids of lower molecular weight were also synthesized.

2. With increase in molecular weight the bactericidal effect toward acid-fast bacteria increased markedly until the higher molecular weight

compounds in the form of their sodium salts were much more effective than the sodium salts of pure chaulmoogric or hydnocarpic acids or the sodium salts of any of the mixed acids from natural oils containing chaulmoogric or hydnocarpic acids.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

CERTAIN Δ^2 -CYCLOPENTENYL ALKYL ACETIC ACIDS AND THEIR ACTION TOWARD *B. LEPRAE*. IX¹

BY JAMES A. ARVIN² WITH ROGER ADAMS

RECEIVED AUGUST 29, 1927

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The effect of the size of the side chain on the bactericidal character of various acids containing the cyclohexyl group was shown in a research described in the preceding paper.¹ The number of carbon atoms present apparently played such an important role in these compounds that it seemed probable that it would play just as important a one certainly in other series of acids, and probably in other classes of compounds now being studied in this same field.

Perkins³ prepared Δ^2 -cyclopentenyl alkyl acetic acids in which the alkyl group was ethyl, *n*-propyl, *n*-butyl and allyl, and reported that some of these acids showed sufficient bactericidal action toward *B. Leprae* to warrant clinical testing. Judging from the results on cyclic acids in this Laboratory, by far the most effective compounds in this series should be those in which the alkyl group is octyl, or nonyl, or of even higher molecular weight. Since these substances have not previously been made, a series of Δ^2 -cyclopentenyl alkyl acetic acids has been produced and tested in which the alkyl group varies from *n*-amyl to *n*-nonyl (I).

CH CH

CH—CH(CO₂H)R

I₃

I

The results were exactly those predicted. The bactericidal action increased very rapidly from *n*-amyl to the *n*-nonyl, the *n*-hexyl killing in dilutions of 1:10,000, but the higher molecular weight compounds in very much greater dilutions, 1:150,000 in the *n*-nonyl (Table I).

The compounds were prepared by condensing the sodium derivative of diethyl- Δ^2 -cyclopentenyl malonate with various alkyl halides, preferably in the absence of the alcohol, so that a higher temperature might be reached

¹ Paper VIII in this series, *THIS JOURNAL*, 49, 2934 (1927).

² This communication is an abstract of a portion of the thesis submitted by James A. Arvin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ Perkins and Cruz, *THIS JOURNAL*, 49, 517 (1927).

TABLE I
EFFECT OF CERTAIN ACIDS ON *B. Lepræ*
—Dilutions of sodium salts—

	1	2	5	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200	220	240	260	280	300
Δ^2 -Cyclopentenyl alkyl acetic acids, $C_5H_7CH(R)CO_2H$. R =																												
<i>n</i> -C ₅ H ₁₁	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
<i>n</i> -C ₆ H ₁₃	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
<i>n</i> -C ₇ H ₁₅	—	—	—	—	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
<i>n</i> -C ₈ H ₁₇	—	—	—	—	—	—	—	—	—	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	+	+	+
<i>n</i> -C ₉ H ₁₉	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	+	+	+	+	+	+	+	+	+

and a better yield of product formed. The di-substituted malonic esters were then saponified with alcoholic potash in the usual way and the dibasic acids converted to the monobasic acids merely by heating above the melting point.

The bacteriological work was carried out by Gerald H. Coleman and W. M. Stanley.

Experimental

Diethyl- Δ^2 -cyclopentenyl Malonate.—The procedure for obtaining this ester was a slight modification of that used by Noller and Adams.⁴ Instead of an excess of dry hydrogen chloride, the gas was passed into the redistilled cyclopentadiene until 1 molecular equivalent had been absorbed. The reaction mixture was allowed to stand for two hours at -5° to -10° , and then without distillation was added to 1.25 molecular equivalents of sodium malonic ester in absolute alcohol. The conditions of condensation were described in a previous paper.⁴ The ester was isolated in the usual way. The yield of the product boiling at $113-118^\circ$ under 5 mm. was 80–85% of the theoretical.

Diethyl- Δ^2 -cyclopentenyl Alkyl Malonate.—After preparing the sodium derivative of diethyl- Δ -cyclopentenyl malonate in the usual way from 5.8 g. of sodium, 175 cc. of absolute alcohol and 56.5 g. of diethyl- Δ^2 -cyclopentenyl malonate, 135 cc. of alcohol was distilled off from the mixture. The alkyl bromide (0.3 mole) was then added and refluxing was continued for forty-eight hours. The rest of the alcohol was then distilled and water added to dissolve the sodium bromide. The products were then isolated in the usual way. The yields of the di-substituted esters from *n*-amyl to *n*-nonyl inclusive were, respectively, 37, 39, 35, 34 and 42% of the calculated amount. There was always recovered from 45–50% of pure diethyl- Δ^2 -cyclopentenyl malonate unchanged.

TABLE II
 $C_5H_7C(CO_2C_2H_5)_2R$, DIETHYL- Δ^2 -CYCLOPENTENYL ALKYL MALONATES

R =	B. p., °C.	n_D^{20}	d_4^{20}	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
<i>n</i> -C ₅ H ₁₁	133–136 (3 mm.)	1.4580	0.9981	68.94	69.01	9.48	9.83
<i>n</i> -C ₆ H ₁₃	150–155 (4 mm.)	1.4572	.9867	69.60	69.89	9.75	10.06
<i>n</i> -C ₇ H ₁₅	159–164 (3 mm.)	1.4582	.9791	70.32	70.89	9.94	9.94
<i>n</i> -C ₈ H ₁₇	169–174 (4 mm.)	1.4591	.9765	70.93	70.63	10.12	10.31
<i>n</i> -C ₉ H ₁₉	183–187 (5 mm.)	1.4595	.9756	71.53	71.81	10.29	10.53

Δ^2 -Cyclopentenyl Alkyl Acetic Acids.—A solution of 17 g. of potassium hydroxide in 75 cc. of alcohol was refluxed on a steam-bath with 0.1 mole of pure diethyl- Δ^2 -cyclopentenyl alkyl malonate for twenty-four hours. The reaction mixture was then

⁴ Noller with Adams, THIS JOURNAL, 48, 1080 (1926).

diluted with 60 cc. of water and distilled until the temperature of the mixture reached about 98°. The residue was refluxed for two hours. It was then cooled to 10° and acidified with concd. hydrochloric acid, using Congo Red paper as an indicator. The malonic acid was separated and the aqueous liquors were extracted with ether. The separated malonic acid was also dissolved in the ether, the ether solutions mixed and dried with calcium chloride and then the ether evaporated. The residue was heated in a round-bottomed flask with an air-cooled reflux condenser for two hours at 160–165°. The residue was distilled under diminished pressure and the yields of the five monobasic acids from *n*-amyl to *n*-nonyl were, respectively, 70, 51, 55, 61 and 72% of the calculated amount.

TABLE III
Δ²-CYCLOPENTENYL ALKYL ACETIC ACIDS

Acids	B. p., °C.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
C ₅ H ₇ CH(<i>n</i> -C ₅ H ₁₁)CO ₂ H	142–145 (5 mm.)	1.4659	0.9629	73.39	73.41	10.27	10.59
C ₅ H ₇ CH(<i>n</i> -C ₆ H ₁₃)CO ₂ H	150–155 (5 mm.)	1.4671	.9573	74.21	73.88	10.56	10.73
C ₅ H ₇ CH(<i>n</i> -C ₇ H ₁₅)CO ₂ H	162–165 (4 mm.)	1.4683	.9499	74.93	75.18	10.78	11.05
C ₅ H ₇ CH(<i>n</i> -C ₈ H ₁₇)CO ₂ H	170–173 (4 mm.)	1.4687	.9452	75.58	76.19	10.99	11.43
C ₅ H ₇ CH(<i>n</i> -C ₉ H ₁₉)CO ₂ H	173–176 (3 mm.)	1.4690	.9436	75.80	76.10	11.13	11.12

Summary

1. Δ²-Cyclopentenyl alkyl acetic acids where the alkyl varies from *n*-amyl to *n*-nonyl have been prepared.
2. The bactericidal action toward *B. Leprae* has been shown to increase rapidly with increase in molecular weight of the alkyl group.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF SASKATCHEWAN]

STUDIES IN URETHANS. IV. ACYL DI-URETHANS AND THEIR REACTIONS WITH AMMONIA AND AMINES¹

BY S. BASTERFIELD, ESLI L. WOODS AND MYRON S. WHELEN

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In a study of guanidine derivatives, Nencki² observed that dicarbethoxyguanidine was decomposed by alcoholic ammonia at 100° into monocarbethoxyguanidine and urethan. Malonyldi-urethan was found by Conrad and Schulze³ to be decomposed by the same reagent into malonamide, ammonium barbiturate and urethan. In neither of these reactions was a urethan grouping converted into a urea as might have been expected. The products obtained by Conrad and Schulze show that from some molecules of diurethan both urethan groups were removed, while from others only one was removed, and the carbethoxymalonamide so formed then condensed to barbituric acid.

The action of ammonia and amines on carbonyldi-urethan has been

¹ A preliminary version of this paper was received July 19, 1926.

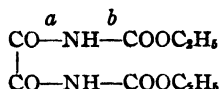
² Nencki, *Ber.*, 7, 1588 (1874).

³ Conrad and Schulze, *Ber.*, 42, 729 (1909).

studied by Dains and his associates.⁴ They report that with aqueous ammonia both amide formation and loss of carbethoxy groups by hydrolysis take place, the main products being carbethoxy-biuret and allophanic ester. Some cyanuric acid and traces of biuret were also found, but apparently no urethan. With aqueous ethylamine, allophanic ester was obtained in 80% yield, and the reaction is interpreted as hydrolysis of a carbethoxy group. With aniline at temperatures from 110 to 170°, a great variety of compounds was obtained, indicating several possible modes of fission of the di-urethan molecule, as well as secondary reactions.

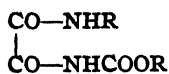
In the present study, oxalyl-, malonyl- and phthalyl-di-urethans have been found to have a strong tendency to lose urethan groups under the action of ammonia and amines, both in aqueous and non-aqueous media, and we regard the reaction as a general one of ammonolysis. Some experiments with carbonyldi-urethan and solutions of ammonia and ethylamine both in water and alcohol also indicate that the interpretation of Dains and his collaborators regarding the loss of carbethoxy groups by hydrolysis is not adequate. Doubtless there is some hydrolysis with aqueous reagents, but the presence of urethan and ethylurethan among the products of decomposition can only be explained by ammonolysis.

It is of interest to consider whether a urethan group is removed as a unit, fission taking place at *a* in the formula below, or whether a carbethoxy group is removed and converted into urethan by splitting of the molecule at *b*.

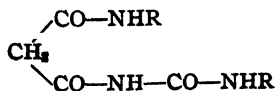


Reactions with ammonia cannot settle this point, since the results may be interpreted either way. Reactions with substituted ammonias, however, show that the first alternative represents the predominant mode of decomposition for oxalyl-, malonyl- and phthalyl-di-urethans. For example, with aqueous ethylamine at room temperature, both oxalyl- and malonyldi-urethans gave the di-ethylamides in large yield and urethan. If the carbethoxy groups had been removed by ammonolysis then the products should have been the unsubstituted amides and ethylurethan.

With aniline at the boiling point there was fairly complete decomposition into the anilides and urethan, the latter being converted by excess of aniline into diphenylurea. At lower temperatures intermediate products of the types



I



II

⁴ Dains, Greider and Kidwell, *THIS JOURNAL*, 41, 1004 (1919).

were obtained in varying quantities, depending on the time of heating and the concentrations of initial components of the reaction. These intermediate products yielded the anilides readily on further heating with aniline and their presence may be regarded as indicative of the course of the reactions.

Further evidence of the removal of urethan groups by ammonolysis was found in an experiment with malonyldibenzyl-di-urethan. This compound was decomposed by alcoholic ammonia at room temperature into malonamide and benzylurethan and by alcoholic ethylamine into diethylmalonamide and benzylurethan.

In none of these experiments with di-urethans was there found evidence of the formation of di-ureas.

The decomposition of carbonyl-di-urethan offers interesting points of contrast with the decomposition of the other di-urethans. Since with ethylamine this compound yields allophanic ester and ethylurethan, among other products, there must be a removal of carbethoxy groups by ammonolysis. The great variety of products obtained by Dains and his collaborators from the reactions of aniline with the di-urethan also indicates a more complex type of decomposition than is found with the di-urethans studied in this Laboratory.

In considering a possible explanation of these facts there are two points to be noted. In the first place, the non-formation of di-ureas and the ready formation of the amides of oxalic, malonic and phthalic acids are significant. With carbonyl-di-urethan and aniline, Dains and his co-workers⁴ observed the formation of carbonyldiphenyl-di-urea, but this is the only instance of di-urea formation. In the second place, the formation of the amides by the removal of urethan groups rather than of carbethoxy groups is especially interesting.

In carbonyl-di-urethan there is present only one kind of acyl radical, that of carbonic acid, while in the other three di-urethans are present, the radicals of much stronger acids in addition to that of carbonic acid. We know nothing of the free energies of formation of either the di-urethans or their products of decomposition but it seems evident that the presence of the radicals of the stronger acids has a very definite influence on the type of decomposition. There seems to be little chance of formation of carbamides except as secondary products when the radicals of stronger acids are present in competition. It may be well to note here that Dains and his collaborators found that methylenedi-urethan and similar compounds were not decomposed by amines even when heated.

Whether the influence of the acid radicals parallels the strength of the corresponding acids cannot be stated as yet. Rough observations on the rates of decomposition of the three di-urethans show that for a given base at a given temperature phthalyl-di-urethan is decomposed most rapidly, oxalyl-di-urethan next, and malonyl-di-urethan least rapidly.

The ionization constants for the four acids involved in the di-urethans considered here are as follows.

TABLE I
IONIZATION CONSTANTS*

	K (first hydrogen)	K (second hydrogen)
Carbonic acid	3.0×10^{-7}	3.0×10^{-11}
Oxalic acid	3.8×10^{-2}	4.9×10^{-3}
Malonic acid	1.6×10^{-3}	2.1×10^{-8}
Phthalic acid	1.2×10^{-3}	3.1×10^{-8}

* Landolt-Börnstein Tabellen.

Experimental Part

Oxalyldi-urethan, $(\text{CONHCOOC}_2\text{H}_5)_2$, was prepared by Hantzsch⁶ from oxalic ester and urethan in the presence of sodium ethoxide. It was obtained by Bornwater⁶ in small quantity in cold ether from oxalyl chloride and urethan. In boiling benzene, Bornwater found that carbonyldi-urethan was formed. In the present study the di-urethan was obtained in quantitative yield by mixing oxalyl chloride and urethan in the required proportions without a solvent. The mixture liquefied and hydrogen chloride was rapidly evolved. In the course of a few minutes the liquid became viscous and finally solidified. The solid crystallized from 95% alcohol in pearly plates; m. p. 172° .

Malonyldi-urethan, $\text{CH}_3(\text{CO.NHCOOC}_2\text{H}_5)_2$.—This was prepared by Conrad and Schulze⁷ by heating malonic acid and urethan in acetic anhydride. It was obtained by Backes, West and Whiteley⁷ by warming together malonic acid, urethan and phosphoryl chloride at 80° ; yield, 71%. In the present study it was readily obtained in 85% yield by refluxing malonyl chloride and urethan in required proportions in benzene until hydrogen chloride was no longer evolved; white, sandy crystals from alcohol; m. p. 124° .

Phthalyl-di-urethan, $\text{C}_6\text{H}_4(\text{CONHCOOC}_2\text{H}_5)_2$.—Phthalyl chloride and urethan in required proportions were heated together at 130° until evolution of hydrogen chloride had ceased. The mixture solidified on cooling and the solid was recrystallized from alcohol; yield, 60%; fine, crystalline powder of slight aromatic odor. The substance softens at 80° and gradually decomposes as the temperature is raised.

Refluxing the acid chloride and urethan in boiling benzene for many hours gave poor results.

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6$: N, 9.09. Found: 9.28, 9.36.

Oxalyldi-urethan

1. ACTION OF AMMONIA.—Oxalyldi-urethan was treated with cold, concentrated, aqueous ammonia. An insoluble, white powder was rapidly formed which was identified as oxamide. The filtrate on evaporation yielded urethan and a little urea.

When dry ammonia gas was passed over the di-urethan heated to 90 – 100° in a water-jacketed tube, a sublimate of urethan was formed in the cooler part of the tube in the course of half an hour.

2. ACTION OF ETHYLAMINE.—The di-urethan was mixed with 33% aqueous ethylamine in the proportion of one to six molecular equivalents and the mixture allowed to stand in a corked flask for twenty-four hours. A precipitate of fine needles was then filtered off and the substance identified as di-ethyloxamide, m. p. 176° . The

⁶ Hantzsch, *Ber.*, 27, 1250 (1894).

⁶ Bornwater, *Rec. trav. chim.*, 31, 105 (1912).

⁷ Backes, West and Whiteley, *J. Chem. Soc.*, 119, 371 (1921).

amount was 70% of the theoretical. From the filtrate, after evaporation at 50–60°, was obtained urethan with a few drops of oil which was not identified.

3. ACTION OF ANILINE.—(a) At 190 and 150°. Mixtures of six molecular equivalents of aniline to one of di-urethan were heated for one and a half hours at the stated temperatures. The solid mass obtained after the reaction mixtures were allowed to cool was extracted with hot alcohol. The insoluble residue was oxanilide (m. p. 244–245°) in almost quantitative yield. The alcohol extract gave several crops of diphenylurea (m. p. 236°).

(b) At 100°. The solid product from a reaction at this temperature contained oxanilide in 60% yield. The alcohol extract gave a product which after many recrystallizations finally yielded a small fraction melting at 136–137°. A much larger amount of this substance was obtained by heating the reaction mixture for only half an hour. At the end of this time there was considerable unchanged di-urethan, but it was quite easy to separate the new product from it. The substance is apparently α -carbethoxy- β -phenyloxamide, $C_6H_5NHCOCONHCOOC_2H_5$. It is rapidly decomposed by aqueous ammonia at room temperature yielding phenyloxamide (m. p. 224°).

Anal. Calcd. for $C_{11}H_{13}N_3O_4$: N, 11.86. Found: 11.84, 11.86, 12.02.

There was no diphenylurea found in the reaction mixture at this temperature but monophenylurea and urethan were isolated. The last named was obtained by extracting the solid reaction product with water. The aqueous extract was evaporated and the brownish, crystalline residue recrystallized from ligroin. The purified substance melted at 48° and was identified as urethan.

Malonyldi-urethan

1. ACTION OF AMMONIA.—Malonyldi-urethan left in contact with concentrated aqueous ammonia at room temperature yielded malonamide, ammonium barbiturate and urethan. This result was similar to that of Conrad and Schulze³ who decomposed the di-urethan with hot alcoholic ammonia.

The di-urethan was not decomposed by dry ammonia at 100°, as was oxalyldi-urethan.

2. ACTION OF ETHYLAMINE.—The reaction was carried out as with oxalyldi-urethan except that the mixture was allowed to stand for one week. Evaporation of the mixture to small volume at 60° gave large, waxy crystals of di-ethylmalonamide in 92% of the theoretical yield. The substance was identified by a mixed-melting-point determination with a known sample of the amide.

3. ACTION OF ANILINE.—(a) At 190°. The reaction was carried out as with oxalyldi-urethan. The solid product was dissolved in hot alcohol. Several fractions of crystals melting at 201–202° were obtained. This material was finally separated by fractional crystallization into malonanilide, m. p. 223°, and diphenylurea, m. p. 236°. No other compound was present.

(b) At 150°. The solid product obtained after two hours' heating was extracted with hot alcohol and the mixture filtered. The filtrate contained malonanilide and diphenylurea. The relatively insoluble residue was finally dissolved in a large volume of boiling alcohol from which it separated on cooling in masses of silky needles, m. p. 234–235°. The substance was not decomposed in the cold by ammonia, but was transformed on being warmed with aniline for half an hour into malonanilide and diphenylurea. It was apparently α -phenyl- β -phenylcarbamyilmalonamide (phenylureido-malonylaniline), $C_6H_5NHCOCH_2CONHCONHC_6H_5$.

Anal. Calcd. for $C_{18}H_{15}N_3O_3$: N, 14.14. Found: 13.92, 14.09.

(c) At 120°. At this temperature a larger proportion of the above compound was obtained, with malonanilide and monophenylurea. There was no diphenylurea.

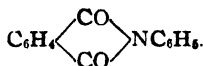
(d) At 100°. Very little change after several hours' heating. Malonyldi-urethan is evidently less sensitive to decomposition by aniline than is oxalyldi-urethan.

Phthalyl-di-urethan

1. ACTION OF AMMONIA.—The diurethan was treated with cold, concentrated, aqueous ammonia. A white, insoluble powder was rapidly precipitated. It was identified as phthalamide, $C_6H_4(CONH_2)_2$, m. p. 220°. Urethan was recovered from the filtrate. The decomposition was quantitative.

Anal. Calcd. for $C_8H_5O_2N_2$: N, 17.07. Found: 17.07.

2. ACTION OF ANILINE.—(a) At 190°. One molecular proportion of di-urethan and four of aniline were heated together for one hour. The solid mass obtained after cooling was extracted with cold alcohol. The extract yielded diphenylurea, m. p. 237°. The more insoluble residue melted at 203° and was identified as phthalanil,



Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.27. Found: 6.08.

(b) At 100°. At this temperature, after the mixture had been heated for thirty minutes, phthalanil was obtained in large amounts and a small quantity of a substance consisting of fine, white needles, m. p. 225°. In order to obtain a larger quantity of this compound a mixture of di-urethan and aniline was heated for only eight minutes. As was expected a considerably greater quantity of the new substance was obtained and much less phthalanil. It was apparently α -phenyl- β -carbethoxyphthalamide, $C_6H_5-NHCOC_6H_4CONHCOOC_2H_5$.

Anal. Calcd. for $C_{16}H_{15}N_2O_4$: N, 8.98. Found: 8.83, 8.98.

The nitrogen content of diphenylphthalamide $C_6H_4(CONHC_6H_5)_2$ is 8.87%, but its melting point is 245°. To eliminate any doubt as to the identity of the new substance, diphenylphthalamide was prepared by the method of Rogow.⁸ The prepared sample melted at 245° and a mixture of it with the substance melting at 225° melted at 200°. It seems safe to conclude that the new substance is the product resulting from the removal of one urethan group by the action of aniline.

Carbonyldi-urethan

In view of the results obtained by the action of ammonia and ethylamine on oxalyldi- and malonyldi-urethans, and also because Dains and his associates make no mention of finding urethan in their study of the decomposition of carbonyldi-urethan, we made a few experiments with the latter substance to determine if urethan was a product of its decomposition by ammonia and ethylamine. (Cf. Decomposition of Dicarbethoxyguanidine.)⁹

1. ACTION OF AMMONIA.—Two and four-tenths grams of the di-urethan was mixed with concentrated aqueous ammonia and allowed to stand at room temperature for three days. One gram of allophanic ester (m. p. 192°) was separated by filtration and the filtrate evaporated on the steam-bath. From the solid residue 0.2 g. of pure urethan was isolated. The remainder was allophanic ester and urea and a small quantity of a substance which did not melt below 300°, and which was probably cyanuric acid. Traces of biuret were also found.

⁸ Rogow, *Ber.*, 30, 1442 (1897).

⁹ Basterfield and Paynter, *THIS JOURNAL*, 48, 2176 (1926).

Somewhat similar results were obtained by heating the di-urethan with alcoholic ammonia under pressure at 100°.

The quantity of urethan isolated was only 20% of the theoretical, but it probably indicates the main trend of the reaction, since urea, biuret and cyanuric acid may be formed through the medium of urethan.¹⁰

2. ACTION OF ETHYLAMINE.—The di-urethan in 33% aqueous ethylamine after standing for four hours at room temperature gave, contrary to expectations, allophanic ester in 75% yield. On longer standing the yield was diminished. In twenty-four hours only 30% of allophanic ester was obtained, and in seventy-two hours the ester had completely disappeared. The clear solution was evaporated in a vacuum, and a residue of oil and crystals was left. The oil was taken up in chloroform and, on being fractionated, yielded a portion boiling at 174–175° which was identified as ethylurethan, $C_2H_5NH-COOC_2H_5$. The crystalline material contained urea and a substance melting at 155° which was not identified.

Some experiments were made on the action of diethylamine on oxalyl- and malonyldi-urethans in alcoholic solution at 100°. After removal of the alcohol by evaporation oils were obtained which, on being fractionated, invariably gave urethan as one of the products. The other products have not yet been identified.

Summary

1. The decompositions of oxalyl-, malonyl and phthalyl-di-urethans by ammonia, ethylamine and aniline have been studied, and the strong tendency for urethan groups to be detached by ammonolysis noted.

2. A comparison with the decomposition of carbonyldi-urethan by the same reagents is made and the different results are indicated.

3. It is suggested that the mode of decomposition of acyldi-urethans is strongly influenced by the nature of the acyl radical. The tendency for urethan groups to be detached may be correlated with a tendency toward the formation of amides of the stronger acids in preference to formation of amides of carbonic acid.

SASKATOON, SASKATCHEWAN, CANADA

NEW BOOKS

General Chemistry. Theoretical and Descriptive. By THOMAS P. MCCUTCHEON, Ph.D., Professor of Inorganic Chemistry, University of Pennsylvania, and Harry Seltz, Ph.D., Assistant Professor of Physical Chemistry, Carnegie Institute of Technology. D. Van Nostrand Company, Inc., 8 Warren St., New York, 1927. x + 415 pp. 33 figs. 22.5 × 14 cm. Price \$3.50.

According to the authors the advantages of the division of general chemistry into two parts, theoretical and descriptive, are:

"Firstly, the student will have at hand a concise and orderly summary of chemical facts, emphasizing the natural groupings and relationships of the elements from the standpoint of the Periodic Law.

¹⁰ Werner, "The Chemistry of Urea," Longmans and Co., New York, 1923, Chaps. 3, 4 and 7.

"Secondly, the student will have available chapters on each of the essential topics of theoretical chemistry, each complete in itself, and free from diverting and irrelevant matter.

"Thirdly, the instructor will have a maximum opportunity to inspire and interest his students by injecting his own method and personality into the course."

A syllabus of lectures is given to suggest a way in which the theoretical and descriptive matter may be combined.

The first 162 pages include all the theoretical material generally included in a text of this kind, and the treatment is excellent. For the sake of brevity, the authors have included almost no historical matter and there are no lists of references in the text. Problems are given at the end of several of the chapters.

Descriptive chemistry, covered in part two, takes up first the more common non-metals, with chapters in order on acids, bases and salts; water, ozone and hydrogen peroxide; valence, equations, nomenclature; and preparation of metals and metallic compounds—classification of salts. The remainder of the elements are taken up in their periodic groupings with a brief discussion of family resemblances at the head of each chapter. It seems to the reviewer that the authors have here missed an opportunity to make their radical treatment really effective. Our modern ideas of atomic structure permit predictions of variations in properties of compounds of elements in the same family, as well as relations with compounds of other elements. It is suggested (p. 11) that, "Similarities in properties of certain groups of elements...are not fortuitous but are a result of a fundamental likeness in the structures of the atoms of these elements." This idea is not carried out to the extent of its possibilities in the discussion of the elements in their periodic groups. Without some such classification, a listing of the properties of elements and compounds seems to the student a hopeless collection of unrelated facts.

The discussions of industrial processes are excellent examples of concise treatment. More figures and illustrations would have added to the appearance of the book.

A. J. SCARLETT, JR.

Quantitative Analysis. By EDWARD G. MAHIN, Ph.D., Professor of Analytical Chemistry in Purdue University. International Chemical Series, H. P. Talbot, Ph.D., Sc.D., Consulting Editor. Third edition. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York; 6 and 8 Bouverie Street, F. C. 4, London; 1924. xvii + 595 pp. 120 figs. 21 × 14 cm. Price \$4.00.

It will always remain a matter of individual opinion how much should be included in a textbook of quantitative analysis. In this book the author

has devoted half the space to the usual simple gravimetric, volumetric and electrolytic determinations, after which he has described in a few chapters methods involving the use of special apparatus, such as the polariscope, calorimeter and refractometer. The rest of the book is devoted to the analysis of industrial products and raw materials, with a chapter on assaying. This part is not complete enough to take the place of more comprehensive reference books. One wonders just what determined the choice of materials so that, for example, paints and varnishes are not mentioned, although oil, fats and waxes are discussed. The reviewer feels that it is a mistake to attempt to write a book on quantitative analysis which is both a textbook and a compendium of industrial methods.

No mention is made of electrometric methods of titration, although it would seem that this subject more properly belongs here than does a chapter on the heat treatment of steel.

The physico-chemical principles involved in analytical processes are not elucidated as fully as might be desired.

Certain errors occur which may be eliminated in a future edition. A few may be mentioned. On p. 78 it is erroneously stated that if aluminum hydroxide is ignited in the presence of ammonium chloride, volatilization of aluminum chloride occurs. On p. 84, from a comparison between the perchlorate and chloroplatinate method for potassium, one would suppose that the former was less accurate and convenient, whereas such is not the case. The statement here and on p. 91 that the preparation of aqueous perchloric acid is dangerous is absurd. It is, however, quite unnecessary to prepare it because C. P. 60% acid has been on the market for years and is no more dangerous than other common acids. The use of 20% acid is a disadvantage not an advantage. On p. 91 it is stated that no definite data on the solubility of sodium perchlorate in alcohol are available. The method suggested for removing ammonium salts by evaporation with sulfuric acid is very undesirable, because it is then necessary to reconvert to chlorides with consequent loss by occlusion. The familiar method of evaporating with nitric and hydrochloric acids is much easier and more accurate. On p. 125 the e. m. f. of the Edison cell is given as 1.6 volts instead of 1.2. On p. 182 the curve for phosphoric acid indicates that this acid cannot be accurately titrated, and this statement is made on the following page, whereas it is a matter of common knowledge that such a titration is possible. In steel analysis no method for V is given, although it is included in the table of contents.

In spite of these criticisms the book contains a wealth of valuable information. It is well written and gives frequent reference to original papers. It contains many well selected problems. It can be recommended as a textbook for elementary and advanced classes.

H. H. WILLARD

Anleitung für das Praktikum in der Gewichtsanalyse. (Laboratory Manual of Gravimetric Analysis.) By DR. R. WEINLAND, o. Professor an der Universität Würzburg. Third enlarged and revised edition. Theodor Steinkopff, Dresden and Leipzig, 1925. viii + 132 pp. 3 figs. 23 × 15.5 cm. Price, unbound, M. 6.

This little book is rather unusual in that it contains nothing about the general operations of gravimetric analysis and only a few pages are devoted to a discussion of the ionization theory, the law of mass action and the method of calculating results. It consists of brief working directions for carrying out 20 simple determinations, 34 separation methods involving ores, alloys, etc., and 13 electrolytic methods. Questions are frequently introduced to call attention to important points and the reactions are well explained. There are abundant references to original papers. One noteworthy feature is the inclusion of many new methods not yet included in reference works on quantitative analysis, as well as some which have never been published elsewhere. Some excellent methods are not mentioned, for example, Starck's method for determining fluorine as PbFCl , and the phenylhydrazine method for aluminum which is widely used in this country. The pyrogallate method is given for bismuth but not for antimony.

Because of the large number of methods described, this book will be found very useful for reference, but as a laboratory text it would need to be supplemented by preliminary lectures or an elementary text.

H. H. WILLARD

Selenium. A List of References, 1817-1925. By MARION FOSTER DOTY. New York Public Library, New York City, 1927. 114 pp. 17.5 × 25.5 cm. Price \$0.65.

Although this book is only intended to contain the titles of works relating to selenium published between 1817 and 1925, and *owned* by the New York Public Library on June 1, 1926, it is apparently a complete index to selenium literature for the period mentioned.

The references in addition to being in chronological order are grouped under the following subjects:

Bibliography	Chemistry
General Works	General and Inorganic
Mineralogy and Crystallography	Organic
Physical and Chemical Constants	Analytical
Electrical and Optical Properties	Biochemistry
Cells and Their Uses	Colloidal Selenium
Other Industrial Applications	Patents

This division of material has given the list of references additional value since with the subject index, the author index and the patent index, the location of an individual article is made particularly easy.

Those who find it convenient to use the facilities of the Reference

Department of the New York Public Library will find the Library Catalog Reference Letters given with each item listed.

There is little doubt that this publication will prove to be a great help to those who are interested in selenium research.

V. W. MELOCHE

Indicators: Their Use in Quantitative Analysis and in the Colorimetric Determination of Hydrogen-Ion Concentration. By DR. I. M. KOLTHOFF, Conservator of the Pharmaceutical Laboratory of the State University, Utrecht. Translated by N. Howell Furman, Ph.D., Assistant Professor of Analytical Chemistry, Princeton University, Princeton, New Jersey. John Wiley and Sons, Inc., 440 Fourth Avenue, New York; Chapman and Hall, Limited, London; 1926. xii + 269 pp. 23 figs. 23.5 × 15 cm. Price \$3.50.

This book discusses fully the theory of neutralization, hydrolysis, buffer action, amphoteric compounds, determination of P_H , titrations and related phenomena. The mathematical treatment is ample. The use of indicators in determining the P_H of solutions and in titrations is described in detail both from a practical and theoretical standpoint; also the use of indicator papers. The theory of the color change of indicators and the effects of alcohol, neutral salts and proteins are fully discussed. There is an interesting chapter on the practical applications of indicator methods. Few errors appear. At the top of p. 142 the Sørensen buffer should be made up using 1/15 mole of Na_2HPO_4 instead of 1/10. On p. 130, line 19, "Exsiccator" should be replaced by "desiccator." The term "table salt" is used frequently instead of "sodium chloride."

This book is well written and should be available to all who have occasion to do any work in this field.

H. H. WILLARD

Abridged Scientific Publications from the Kodak Research Laboratories. Vol. X, 1926. The Eastman Kodak Company, Rochester, New York, 1926. 247 pp. Illustrated. 17 × 24 cm.

This valuable booklet contains the essential material of thirty-eight papers previously published in seventeen journals, scientific and industrial. It serves alike to propound major problems of present-day photography and to record the progress being made toward their solution. The critical discussion of reports from other laboratories contributes not a little to the picture.

While such titles as "Flocculation and Deflocculation of the Silver Halides" and "Simplified Deduction of the Doppler Effect for Elliptic Space" duly represent the theoretical aspects of the science, there is a preponderance of articles of lively interest and immediate value to practical photographers or even to unskilled amateurs. The problems of the

motion picture industry, also, receive considerable attention. Especially suggestive to moderately advanced workers are "Characteristics and Anomalies of Emulsions on Development," "Contrast of Photographic Printing Paper" and "On the Relation between Time and Intensity in Photographic Exposure, IV."

The Abridged Scientific Publications are worthy of wide distribution and careful study.

G. S. FORBES

Principles of Organic Chemistry. By DAVID E. WORRALL, Ph.D., Professor of Organic Chemistry in Tufts College. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1927. xii + 312 pp. 20.5 × 14 cm. Price \$2.50.

We already have a number of excellent and highly satisfactory textbooks of organic chemistry, and they are being kept up to date. This good book is a further addition to the list.

It begins, we believe unfortunately, with a study of alcohols. On page one are given the two possible structural formulas of ethyl alcohol, followed immediately by the structures of higher alcohols. It seems to me that this is a very heavy dose for the beginner. Organic Chemistry is quite difficult for beginners during the early stages of its study and hard enough even when we begin with the simplest of hydrocarbons, methane. The statement is made that alcohols are the subject of the first chapter because "in actual (laboratory) practice one starts with an oxygen-containing compound." However, some of the best laboratory manuals begin with the preparation of methane. Theoretically and practically this leads on easily and logically to the halides and then to the alcohols; and I think we can also say that students are more familiar nowadays with "gas" than with alcohol. Neither do I like the order of the other subjects in the aliphatic series. Of the several arrangements used by writers, however, no one can be dogmatically called the best.

The statements throughout the book are very carefully made and the book is very readable.

ALVIN S. WHEELER

Neue Methoden der Organisch-Chemischen Analyse. (New Methods of Organic Analysis.) By H. TER MEULEN, Professor at the Technical High School of Delft, and Dr. J. HESLINGA. Akademische Verlagsgesellschaft m. b. H., Leipzig, Germany, 1927. v + 49 pp. 22 figs. 15 × 21 cm.

This interesting booklet presents detailed directions for the quantitative estimation of carbon, hydrogen, oxygen, nitrogen, sulfur, the halogens, arsenic and mercury in organic compounds. Special attention has been given to the determination of nitrogen in coal and in coke, and to

methods for estimating the sulfur content of petroleum and petroleum products. While some modifications of the standard oxidation combustion methods are given, the novelty in most of the methods presented lies in the extensive use of catalytic hydrogenations. Approximately one-third of the pages are devoted to a direct method for the determination of oxygen, together with modifications of the procedure needed when nitrogen, sulfur, the halogens and other elements, interfering with the smooth running of the process, are present. By hydrogenation in the presence of nickel, the carbon is converted to methane, and the oxygen to water which is collected and weighed.

While, in all probability, few of these methods will supplant those now in general use, it is refreshing to find investigators attempting reasonable, if radical, advances in the field where the classic work of Liebig and Dumas was accomplished.

G. ALBERT HILL,

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DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE SOLUTIONS

BY GÖSTA ÅKERLÖF

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I. Introduction

Higher velocities of catalyzed reactions in solutions of electrolytes have seldom been measured on account of rapidly increasing experimental difficulties. Using titration methods in some cases it may be possible to obtain relatively accurate results for reaction velocities with a half period as low as 150 seconds. This was shown by the measurements of Harned and Seltz¹ for the conversion of acetylchloro-aminobenzene to *p*-chloro-acetanilide in solutions of hydrochloric acid. A purely physical method for velocity measurements has therefore far greater possibilities because it eliminates the taking of samples, which necessarily involves a large waste of time. In the following will be given the results of some measurements of the decomposition of diacetone alcohol in concentrated alkali hydroxide solutions. It was found possible to obtain reasonably accurate results up to reaction velocities with a half period of about 35 seconds. For still higher velocities the difference between the calculated values and those obtained with the apparatus used increased rapidly with increasing alkali hydroxide concentration. This was because the temperature changes caused by the reaction could not be counteracted rapidly enough.

With the method for measuring these higher velocities worked out in detail, it was possible to study various questions of great theoretical interest. Electromotive-force measurements of Harned² for mixtures

¹ Harned and Seltz, *THIS JOURNAL*, **44**, 1475 (1922).

² (a) Harned, *ibid.*, **48**, 326 (1926); compare further (b) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

of hydrochloric acid or the alkali hydroxides with the alkali chlorides at constant total molarity in aqueous solutions have shown that the logarithm of the activity coefficient of the acid or hydroxide varies directly as their respective concentrations. As Harned^{2b,3} has also shown that a number of the ions of these electrolytes show a distinct additive behavior, it would seem to be most probable that this relationship is also valid for the single ions of the acid or the alkali hydroxides. It was found by Åkerlöf⁴ that the decomposition velocity of diacetone alcohol in alkali hydroxide-alkali salt solutions is additive and always seemed to follow the activity of the hydroxyl ion as long as counteracting influences did not interfere. Therefore it was of considerable interest to measure the decomposition velocity in alkali hydroxide-salt solutions at constant total molarity over a wider concentration range. Just as for the electromotive-force measurements, here also a linear variation was found.

With varying constant total molarity a number of straight lines were obtained which seemed to be parallel within the experimental errors. The extension of these lines to zero salt concentration gave the logarithm for the pure hydroxide solution. Thus a method had been found of predicting experimentally with a certain degree of accuracy the decomposition velocity which would be expected for a pure hydroxide solution of a given concentration. It also was found that the thermodynamic activity of the alkali hydroxide present in the pure hydroxide solution was proportional to the reaction velocity. The values predicted from the activity function on the one hand and those from the constant molarity curves on the other agreed very well. Therefore it was possible to decide when the method used for the velocity measurements began to break down or at least when the accuracy of the results obtained might be suspected.

II. Experimental Methods

For reaction velocities up to $K = 0.1$ corresponding to a half period of three minutes, the experimental method used was in every detail the same as previously described. At higher velocities the trouble began. With increasing reaction velocities it was necessary to increase the amount of diacetone alcohol used in order to have enough left when the measurement could be started. However, at the same time it was found that the different values obtained for the velocity constant from a single run always showed a continuous decrease as the reaction proceeded toward its completion.

TABLE I

TEMPERATURE CHANGES DURING THE DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE SOLUTIONS

Time, min.....	0.00	0.30	1.30	2.30	3.30	4.30	5.30	6.30	7.30	∞
Temperature.....	3.042	2.871	2.480	2.240	2.071	1.965	1.887	1.831	1.086	1.720
$K \times 10^6$ (sec.)....	...	(201)	267	270	274	271	272	276	270	...

² (a) Harned, *THIS JOURNAL*, **42**, 1808 (1920); (b) *Z. physik. Chem.*, **117**, 1 (1917).

⁴ Åkerlöf, *THIS JOURNAL*, **48**, 3046 (1926).

A detailed study of the heat of solution for the diacetone alcohol and the heat of reaction for its decomposition gave a clear conception of the difficulties encountered. When 5 cc. of diacetone alcohol at ordinary temperatures was dissolved in 100 g. of water, the temperature was found to increase 1.54 degrees. In an alkali hydroxide solution the heat of solution must be very nearly the same as in pure water and therefore in this case also an immediate increase was first observed. The temperature then began to drop, soon passed through the starting point and finally reached a value 0.19 degree lower. Table I gives a summary of some calorimetric measurements of the temperature changes using a Beckmann thermometer.

About 25 cc. of diacetone alcohol had been mixed with 520 g. of approximately 1 *N* sodium hydroxide in the silver foil solution vessel of the calorimeter. This was well heat-insulated and the temperature changes due to stirring amounted to about 0.005° in five or six minutes. Therefore only the end value has been given a slight correction. With increasing velocity the Beckmann thermometer is soon completely unable to follow the rapid temperature changes but it is possible that a method could be worked out with photographic registration of resistance changes for a thin wire or the electromotive-force changes for a set of thermocouples immersed in the solution.

With the apparatus available the following procedure was adopted for the measurement of higher reaction velocities. The reaction tube (Fig. 1) was evacuated for ten to fifteen minutes. In order to avoid temperature changes in the reaction tube at the start of the reaction due to temperature differences between the water pump belonging to the thermostat system and the water in the thermostat, this pump was started during the evacuation of the tube about five minutes before the diacetone alcohol was mixed with the solution to be used for the measurement. The running of the water pump usually caused a very slow temperature increase of 0.01 to 0.02° during the entire run of the measurement. The magnitude of the temperature change varied somewhat with the room temperature. The amount of water passed through the spiral in the reaction tube was approximately 1000 cc. a minute and the spiral had 30 complete windings on a total length of 15 inches.

The diacetone alcohol was carefully poured on top of the solution in the mixing vessel, then immediately mixed for a certain number of seconds with the alkali hydroxide solution with a very efficient high-speed stirrer. The filling of the reaction tube

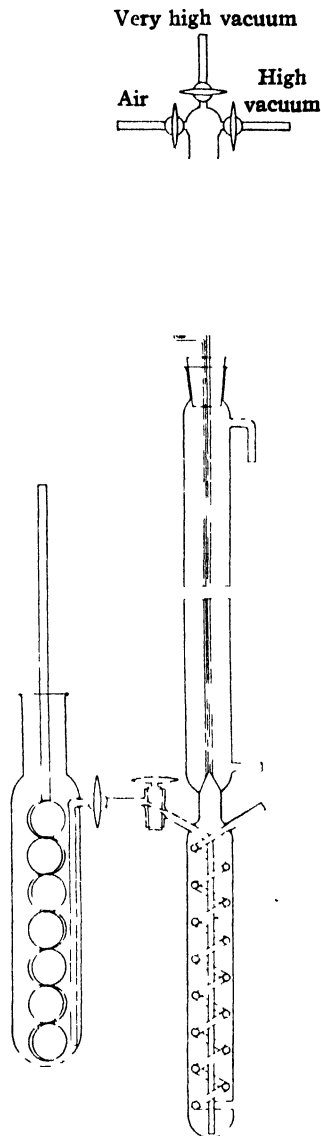


Fig. 1.—Apparatus used for the determination of higher velocities for the decomposition of diacetone alcohol in alkali hydroxide solutions.

started the moment the stirrer stopped. After five seconds the tube was filled to eight or nine tenths. Then the filling was stopped in order to let some of the foam disappear. When a predetermined number of seconds had passed, the filling was completed, the stopcock to the vacuum line closed and a large drop of mercury drawn in from the supply tube at the top of the capillary. The entire length of the capillary was then kept filled with mercury (about 80 cm. pressure) for a few seconds in order to compress rapidly any tiny gas bubbles in the reaction tube. At last the mercury column was shortened to its usual length and the two stopcocks between reaction tube and mixing vessel were tightly closed. The measurement of the reaction velocity could be started a few seconds later.

After some training it was found that about five seconds were necessary for the setting of the cathetometer to any desired height with an error of less than 0.1 of one mm. The reader⁵ of the stop watch obtained an accuracy of plus or minus one-fifth of one second, but this accuracy was usually unnecessary, when other possible errors are considered. The complete mixing of the diacetone alcohol with the solution could easily be accomplished in ten seconds. For the complete filling of the reaction tube a time of not less than thirty seconds was found to be desirable.

It is easy to understand that this method of measuring high reaction velocities has its difficulties. The solutions foamed violently during the filling of the reaction tube on account of the high vapor pressure of the acetone formed. It was impossible to wait until the greater part of the foam had disappeared and, therefore, a chance had always to be taken that a rapid compression would dissolve the remaining gas bubbles within a few seconds. The spiral in the reaction tube had a relatively large surface. In one way this was a decided disadvantage because it gave such good resting places for gas bubbles. On the other hand, the surface had to be large in order to insure a sufficiently constant temperature.

TABLE II
ATTAINABLE ACCURACY OF THE RESULTS

Solution Time in seconds	with 2 N KOH Catheto- meter	$K \times 10^3$	Solution Time in seconds	with 1.8 N NaOH Catheto- meter	$K \times 10^3$	Solution Time in seconds	with 2.2 N LiOH Catheto- meter	$K \times 10^3$
0.0	8.00	...	0.0	10.00	...	0.0	10.00	...
24.4 ^a	20.00	...	25.4 ^a	20.00	...	25.2 ^a	20.00	...
35.0	24.00	772	39.4	24.00	592	37.2	24.00	642
48.0	28.00	775	55.8	28.00	611	52.0	28.00	637
64.8	32.00	778	66.6	30.00	601	60.8	30.00	636
75.8	34.00	776	78.6	32.00	602	71.0	32.00	634
89.4	36.00	776	92.2	34.00	610	81.6	34.00	648
106.6	38.00	782	110.6	36.00	606	96.2	36.00	643
133.4	40.00	779	136.2	38.00	597	115.0	38.00	636
183.6	42.00	787	174.2	40.00	595	141.0	40.00	629
∞	43.3	...	∞	43.0	...	∞	44.6	...

^a Used as starting time for the calculation.

^b The large number of very rapid, consecutive time readings required the utmost attention. The author is highly indebted to Dr. C. C. French, who made all the time readings for more than 150 high-velocity measurements. The author wishes also in this place to express his most sincere thanks to Dr. French.

The constancy of temperature could not be directly determined but the temperature changes during the measurement itself must naturally have been very small, as only the very last part of the reaction was measured. It was, however, another possible chance that had to be taken. It might then appear that the only way to test the possible value of the method and the efficiency of the apparatus used was to see whether constant and reproducible results could be obtained. Table II gives the summary of a few measurements.

The measurements given in Table II may seem to indicate a fairly high accuracy for the results obtained. However, it was found that at velocities with half periods of less than thirty seconds the deviation between measured and calculated velocities increased rapidly, although the measurements showed a high degree of constancy and were easily reproducible. Table III gives a summary of some measurements with 3, 3.5 and 4 *N* sodium hydroxide solutions.

TABLE III
MEASUREMENTS OF VERY HIGH REACTION VELOCITIES

Solution with 3 <i>N</i> NaOH			Solution with 3.5 <i>N</i> NaOH			Solution with 4 <i>N</i> NaOH		
Time in seconds	Catheto-meter	$K \times 10^4$	Time in seconds	Catheto-meter	$K \times 10^4$	Time in seconds	Catheto-meter	$K \times 10^4$
0.0	10.00	...	0.0	10.00	...	0.0	10.00	...
14 ^a	20.00	...	11.0 ^a	20.00	...	11.6	20.00	161
21	24.00	104	16.0	24.00	128	18.0	24.00	162
29	28.00	108	22.2	28.00	125	22.0	26.00	162
40	32.00	105	29.0	32.00	128	26.8	28.00	161
53	36.00	108	38.6	36.00	126	32.6	30.00	160
74	40.00	108	51.0	40.00	127	39.6	32.00	161
91	42.00	108	71.0	44.00	126	48.6	34.00	163
115	44.00	101	86.6	46.00	129	61.6	36.00	169
∞	45.8	...	∞	49.1	...	∞	38.6	...
K observed, 0.636			K observed, 0.761			K observed, 0.974		
K calculated, 0.69			K calculated, 0.85			K calculated, 1.09		

^a Used as starting time for the calculation.

The measurements given in Table III were obtained with a larger reaction tube having two spirals. The water velocity was very high. The infinity values always decreased slowly after they had reached their highest point. This maximum point was used as infinity value. The differences between observed and calculated values increase rapidly with increasing concentration of the alkali hydroxide. This apparently must be due to the inefficiency of the apparatus used. The temperature changes of the solution due to the reaction follow the same formula that was used for the calculation of the reaction velocity. The velocity with which the temperature of the solution in the reaction vessel comes back to the temperature of the water in the thermostat also follows this formula (Newton's cooling law). As long as the velocity for this heat exchange between

water and solution can follow the velocity for the temperature changes of the solution from the heat of reaction the observed expansion ought to give a true expression for the decomposition velocity of the diacetone alcohol. When this velocity increases beyond a certain limit, the velocity constants obtained must be too low, because the temperature decreased during the reaction.

III. Experimental Results with Aqueous Solutions of Potassium, Sodium and Lithium Hydroxide

A summary of the measurements with these solutions is given in Table IV. All concentrations are given in weight normality. For hydroxide concentrations of 0.8 and higher, the amount of diacetone alcohol used was about 5% of the total volume of the solution. The average error of the velocity constants is difficult to judge for the highest concentrations. Up to an hydroxide concentration of 1.6 *N* it may not exceed 2 or 3% unless there are unknown systematic errors. The velocity constants are given with the minute as the unit of time. In order to show how rapidly the experimental difficulties are increasing with increasing hydroxide concentration, the half period of reaction is given in seconds, *T*, for potassium hydroxide solutions.

TABLE IV

DECOMPOSITION VELOCITY FOR DIACETONE ALCOHOL IN SOLUTIONS OF POTASSIUM, SODIUM AND LITHIUM HYDROXIDE

Concn. in wt. norm. <i>N</i>	KOH solutions			NaOH solutions		LiOH solutions	
	<i>K</i>	<i>T</i>	<i>K/N</i>	<i>K</i>	<i>K/N</i>	<i>K</i>	<i>K/N</i>
0.1	0.0211*	851	0.211	0.0208*	0.208	0.0205	0.205
.2	.0402	449	.201	.0392	.196	.0384	.192
.4	.0790	229	.198	.0758	.189	.0732	.183
.6	.117	154	.195	.112	.187	.107	.178
.8	.154	117	.192	.149	.186	.139	.175
1.0	.196	92	.196	.186	.186	.174	.174
1.2	.246	74	.205	.227	.190	.210	.175
1.4	.293	62	.209	.268	.191	.245	.175
1.6	.347	52	.217	.314	.196	.280	.175
1.8	.402	45	.223	.362	.201	.313	.174
2.0	.468	39	.234	.412	.206	.346	.173
2.2	.542	33	.246	.469	.213	.380	.173

* These values are recently redetermined.

A graphical representation of the reaction velocity as a function of the alkali hydroxide concentration is given in Fig. 2. The figure shows that in solutions up to 1 *N* the velocity is approximately proportional to the hydroxide concentration. Fig. 3 has a much greater interest. Here the ratio between velocity constant and hydroxide concentration is plotted as a function of this concentration.

This ratio shows for lithium hydroxide solutions an almost continuous

decrease, but for solutions of the other two hydroxides it passes through a minimum between 0.6 and 1 *N*, then increases, rapidly for potassium

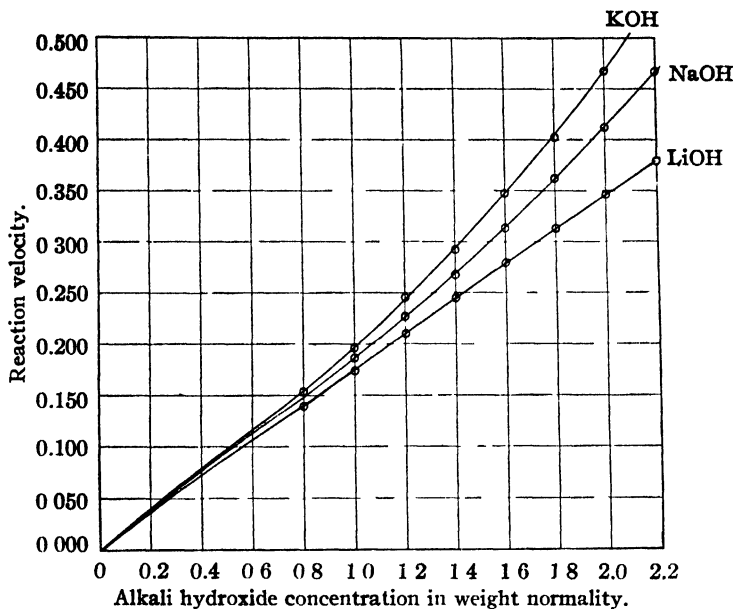


Fig. 2—Curves for the decomposition velocity of diacetone alcohol in aqueous solutions of potassium, sodium and lithium hydroxide.

hydroxide but comparatively slowly for sodium hydroxide solutions. The comparison of the curves in Fig. 4 for the activity coefficients of the alkali

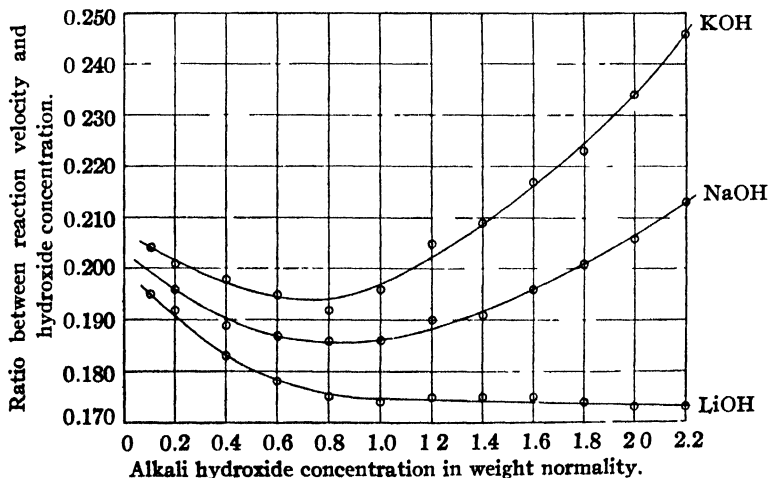


Fig. 3.—Curves for the ratio between concentration and decomposition velocity of diacetone alcohol in aqueous solutions of potassium, sodium and lithium hydroxide.

hydroxides as measured by Knobel,⁶ Harned^{7,8b} and Harned and Swindells,^{8,8b} with the curves for the ratio between decomposition velocity and hydroxide concentration shows they are very similar to each other. For the two sets of curves the minima appear at about the same place and their distribution relative to each other is in both cases approximately the same. The close relationship between activity of the alkali hydroxide present and the decomposition velocity is still more clearly shown in Table V where the ratio between the activity of the alkali hydroxide

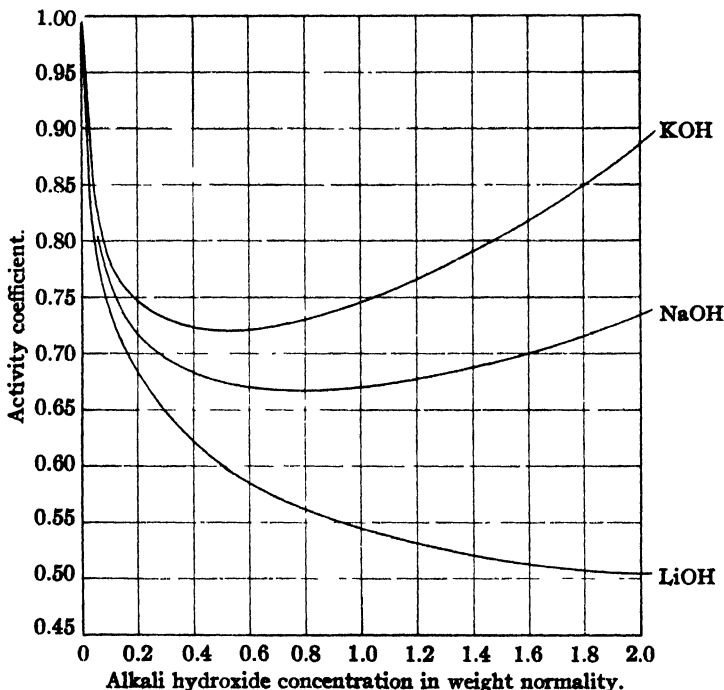


Fig. 4.—Curves for the activity coefficients of the alkali hydroxides in pure aqueous solutions.

and the velocity constant is given. The activity coefficients of the alkali hydroxides were calculated from the following equation

$$\log \gamma_{\text{MOH}} = -\frac{0.354 \sqrt{2m}}{1 + H \sqrt{2m}} + B 2m - \log \left(1 + \frac{w \cdot 2m}{1000} \right)$$

where γ is the activity coefficient, A and B are empirical constants and w is the molecular weight of the solvent. The values of A and B are given in Table V. They were calculated by Harned and Åkerlöf.^{8b}

The ratio between activity and velocity constant for potassium and

⁶ Knobel, *THIS JOURNAL*, **45**, 70 (1923).

⁷ Harned, *ibid.*, **47**, 876 (1925).

⁸ Harned and Swindells, *ibid.*, **48**, 126 (1926).

TABLE V
RATIO BETWEEN ACTIVITY OF THE HYDROXIDE PRESENT AND THE DECOMPOSITION
VELOCITY OF DIACETONE ALCOHOL

Concn. in wt. norm. N	KOH solutions		NaOH solutions		LiOH solutions	
	γ	$\gamma N/K \cdot 10^3$	γ	$\gamma N/K \cdot 10^3$	γ	$\gamma N/K \cdot 10^3$
0.1	0.783	371	0.767	369	0.744	36
.2	.745	371	.716	366	.684	35
.4	.721	364	.685	362	.620	34
.6	.720	384	.669	358	.583	33
.8	.730	375	.666	358	.560	32
1.0	.745	380	.669	360	.542	31
1.2	.767	374	.677	356	.530	30
1.4	.791	378	.687	360	.520	30
1.6	.818	377	.700	357	.513	29
1.8	.849	381	.715	356	.507	29
2.0	.882	377	.732	355	.503	29
	A = 0.777		A = 0.660		A = 0.500	
	B = .0632		B = .050		B = .0215	

sodium hydroxide solutions is apparently a constant within the experimental errors. For lithium hydroxide solutions it varies slightly more and in a definite direction. However, the variations might easily be due to a combination of systematic errors in the velocity determinations and comparatively small errors of two or three millivolts in the electromotive-force measurements. Therefore it would seem to be proved with very little doubt that the decomposition velocity of diacetone alcohol in pure aqueous solutions of the alkali hydroxides is determined by the activity of the hydroxide present.

IV. Measurements at Constant Total Molarity with One Salt Present

The individual activity coefficients of the hydroxyl ion in pure alkali hydroxide solutions are unknown. It seems to be very probable that at a given concentration the activity coefficient of this ion is highest in potassium and lowest in lithium hydroxide solutions, which is the same order as for the ratio between activity of the hydroxide and the velocity constants. The activity coefficients of the cations of the alkali hydroxides change in the opposite order. Therefore it must be improbable that the activity of the hydroxyl ion is the only determining factor in the decomposition velocity of diacetone alcohol. This was also shown in the preceding paper. The compensating effect that must exist to keep the ratio between activity of the hydroxide and the decomposition velocity constant, may partly be caused by changes of the activity of the reacting substance due to the electrical field of the ions present. The presence of the hydroxyl ion is apparently necessary to get the reaction started. To account for the unknown effect it may therefore be assumed that after the start the cations participate to complete the process. In that

case their activity must enter into the velocity function. However, this assumption might bring in another difficulty. The individual activity coefficient of the hydroxyl ion decreases when an alkali halide is added. At moderate salt concentrations this decrease seems to be of the same relative magnitude as the decrease in reaction velocity, although the activity of the cation increases rapidly.

On account of this unknown effect a simple relation between the activity of the hydroxide and the velocity cannot be expected when a salt is added. Harned^{2a} and Harned and Åkerlöf^{2b} have shown that the logarithm of the activity coefficient of hydrochloric acid or the alkali hydroxides in alkali chloride solutions at constant total molarity varies linearly with their concentration. Therefore it seemed that this case would offer the best possibilities for a theoretical interpretation of velocity measurements in alkali hydroxide-alkali salt solutions. A summary of the measurements is given in Table VI.

TABLE VI
VELOCITY MEASUREMENTS AT CONSTANT TOTAL MOLARITY OF 2

MeOH <i>N</i>	KOH-KCl solutions		NaOH-NaCl solutions		LiOH-LiCl solutions	
	<i>K</i>	Log <i>K/N</i>	<i>K</i>	Log <i>K/N</i>	<i>K</i>	Log <i>K/N</i>
0.1	0.0144 ^a	-0.842	0.0123 ^a	-0.910	0.0105	-0.979
.2	.0298	-.827	.0254	-.896	.0213	-.972
.4	.0619	-.810	.0539	-.871	.0454	-.945
.6	.0958	-.797	.0865	-.841	.0716	-.923
.8	.138	-.763	.121	-.820	.101	-.899
1.0	.177	-.752	.161	-.793	.135	-.870
1.2	.229	-.719	.202	-.774	.169	-.851
1.4	.281	-.697	.250	-.748	.211	-.822
1.6	.335	-.679	.293	-.737	.256	-.796
1.8	.392	-.662	.345	-.717	.301	-.777
2.0	.468	-.631	.412	-.686	.346	-.762

^a Interpolated from results published in preceding paper.

A graphical representation of the values for log *K/N* given in Table VI is shown in Fig. 5 as a function of the alkali hydroxide concentration. In Fig. 6 are given the curves for the logarithm of the activity coefficients of the alkali hydroxides in solutions of the corresponding alkali chlorides at the constant total molarity of two. For the plotting of these last curves only two points could be obtained for each one of them but it has been shown by Harned and Åkerlöf that they must be straight lines.

As with the curves for the logarithm of the activity coefficients of the alkali hydroxides, those representing the velocity measurements are straight lines, but there is a great difference in the dispersion of the curves. In the former case they diverge at large angles but in the latter they seem to be very nearly parallel. This was partly to be expected. In Fig. 7 are given the electromotive-force changes for the hydroxyl ion in 0.1 *N* alkali hydroxide solutions at increasing concentrations of the corre-

sponding alkali chlorides according to the calculations of Harned.⁹ The electromotive force is proportional to the logarithm of the activity coef-

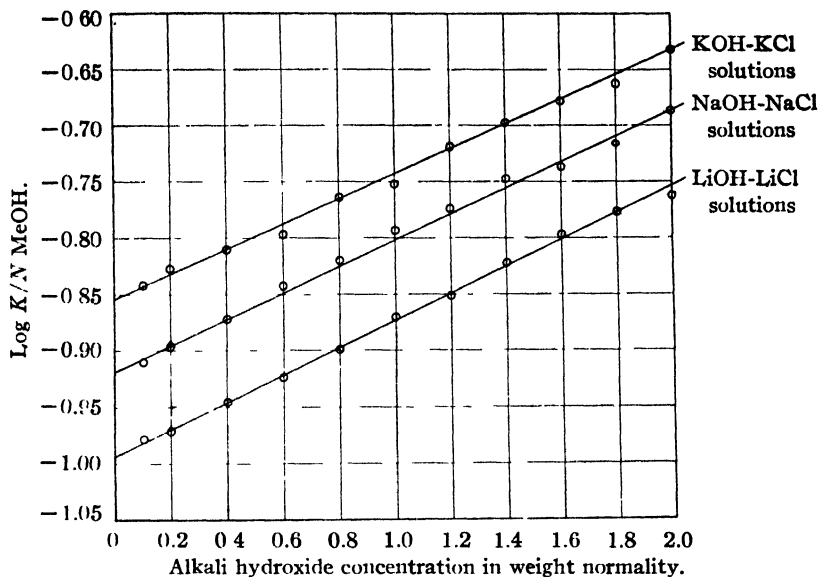


Fig. 5.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in alkali hydroxide-alkali chloride solutions with the constant total molarity of 2.

ficient. Therefore the individual activity coefficients of the hydroxyl ion according to Fig. 7 must have quite different values for the three

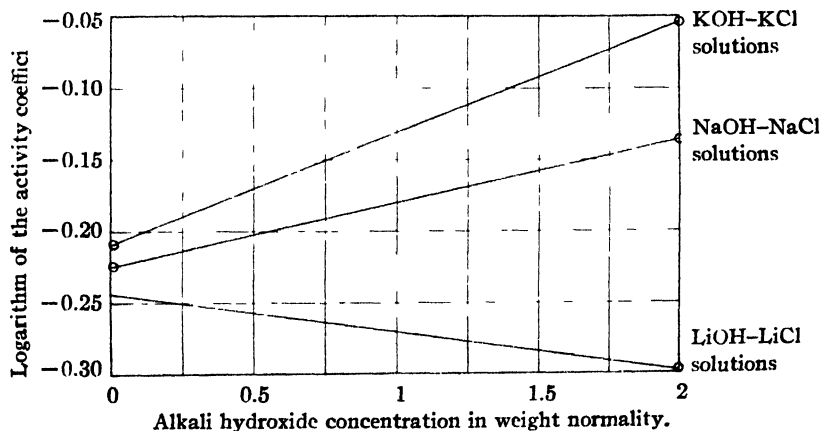


Fig. 6.—Curves for the logarithm of the activity coefficients of the alkali hydroxides in alkali hydroxide-alkali chloride solutions with the constant total molarity of 2.

⁹ Harned, *J. Phys. Chem.*, 30, 433 (1926).

alkali hydroxides at small hydroxide and high salt concentrations. To the electromotive-force differences shown in Fig. 7 should also be added the differences in the pure 0.1 *N* hydroxide solutions since the curves are all referred to the same starting point. This would draw them still further apart. With the simple assumption that the decomposition velocity of diacetone alcohol is proportional to the activity of the catalyzing ion, the difference in distribution for the two sets of curves in Figs. 5 and 6 would be easier to understand.

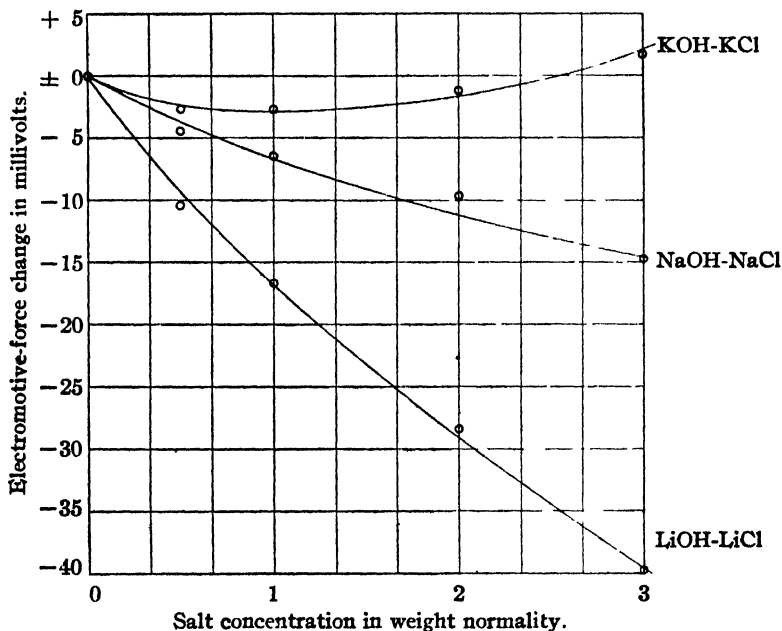


Fig. 7.—Curves for the approximate electromotive-force changes of the hydroxyl ion in 0.1 *N* alkali hydroxide solutions at increasing concentrations of the corresponding alkali chlorides.

However, at present the most important result of the velocity measurements at constant total molarity is that $\log K/N$ varies linearly with the hydroxide concentration. The concentration of the cations of the electrolytes present in these solutions is constant. According to the additivity principle of MacInnes¹⁰ and Harned^{3a,b} for the activity coefficients of strong electrolytes it may then be considered as approximately valid that the activity of the cations is constant. If this approaches the true conditions, the logarithm for the individual activity coefficient of the hydroxyl ion must vary linearly with the concentration of this ion. Since it was found that in addition to the activity of the catalyzing ion there was another factor, as yet unknown, on which the decomposition velocity

¹⁰ MacInnes, *THIS JOURNAL*, **41**, 1086 (1919); **43**, 1217 (1921).

of the diacetone alcohol was dependent, the variations in this factor in solutions of strong electrolytes must follow the same general formulas previously found for the activity coefficient of an ion from electromotive force measurements.

V. Measurements at Varying Constant Total Molarity with One Salt Present

Harned and Åkerlöf have found that the curves for the logarithm of the activity coefficients of the alkali hydroxides in solutions of their corresponding chlorides at varying constant total molarity as a function of the hydroxide concentration are represented by a series of parallel,

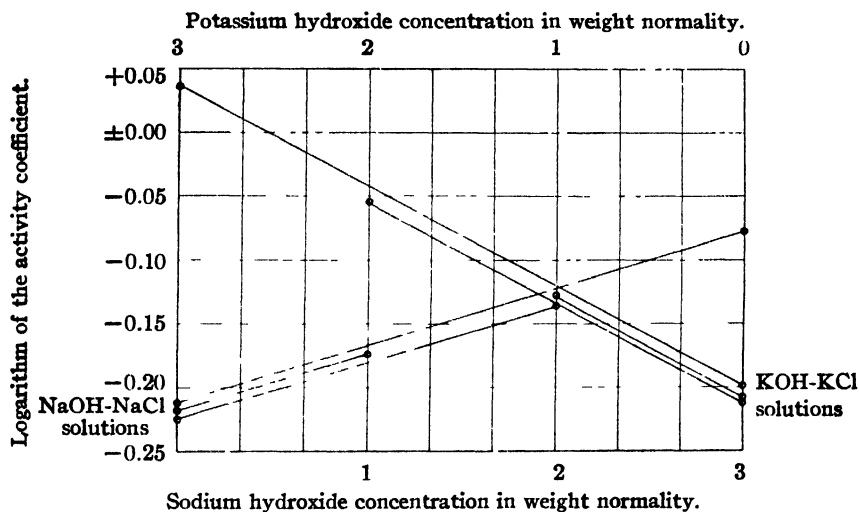


Fig. 8.—Curves for the logarithm of the activity coefficients of potassium and sodium hydroxide in solutions of the corresponding alkali chlorides at varying constant total molarity.

straight lines. This is shown in Fig. 8 for potassium and sodium hydroxide solutions. A summary of the velocity measurements in sodium hydroxide-chloride solutions at varying constant total molarity is given in Table VII.

This table gives the values obtained for $\log K/N$ at the hydroxide concentrations 0.1, 1.0 and 2.0 *N*. A graphical representation of these measurements is shown in Fig. 9. The curves are drawn as straight lines, parallel to each other, except the line for the total molarity of one. The angle for this line with the others is, however, very slight. A comparison of these curves with those for sodium hydroxide-chloride solutions in Fig. 8 shows their relative distribution to be different, which was to be expected. The activity of the alkali hydroxide is determined by the product of the activities of cation and anion. As the function of the cation apparently

TABLE VII

VELOCITY MEASUREMENTS IN SODIUM HYDROXIDE-SODIUM CHLORIDE SOLUTIONS AT VARYING CONSTANT TOTAL MOLARITY

NaOH N	NaCl N	$K \times 10^4$	NaOH N	NaCl N	$K \times 10^4$	Log K/N
0.1	0.5	170 ^a
.1	1.0	149 ^a	0.1	0.9	152 ^b	-0.818
.1	2.0	121 ^a	.1	1.9	123 ^b	-.910
.1	3.0	101 ^a	.1	2.9	102 ^b	-.991
.1	4.0	91.8 ^a	.1	3.9	92 ^b	-1.036
.1	5.0	83.5 ^a	.1	4.9	84 ^b	-1.076
.1	6.0	78.1 ^a	.1	5.9	78 ^b	-1.108

NaOH	NaCl	$K \times 10^4$	Log K/N	NaOH	NaCl	$K \times 10^4$	Log K/N
1.0	0.0	186	-0.730
1.0	1.0	158 ^b	-.802	2.0	0.0	412	-0.686
1.0	2.0	133	-.876	2.0	1.0	342	-.767
1.0	3.0	119	-.924	2.0	2.0	301	-.823
1.0	4.0	109	-.963	2.0	3.0	280	-.854
1.0	5.0	98.8	-1.005	2.0	4.0	264	-.879

^a Values given in preceding paper.

^b Interpolated velocity measurements.

must be a little different from that of the hydroxyl ion, this must give a different distribution of the corresponding curves in the two cases.

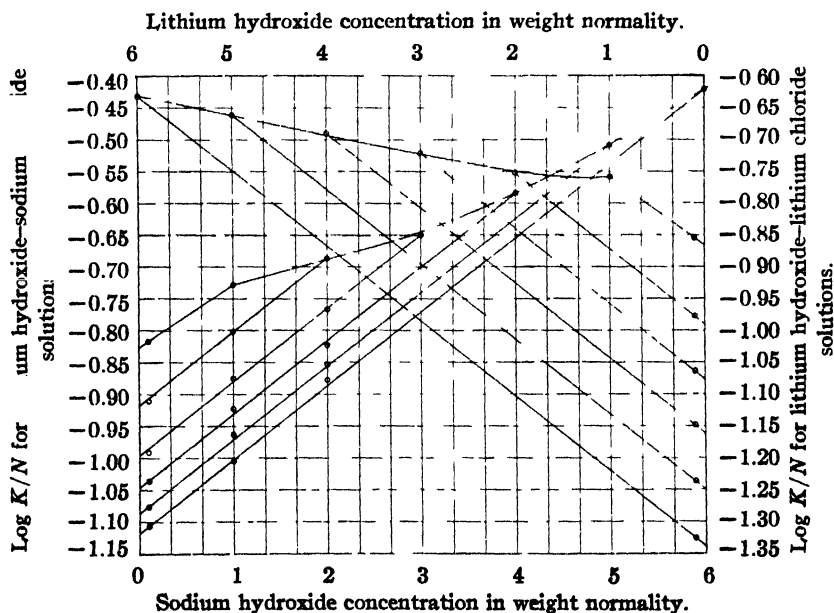


Fig. 9.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in sodium and lithium hydroxide-chloride solutions with varying constant total molarity.

In Fig. 9 all lines are extended to zero salt concentration. This gives graphically the logarithm for the reaction velocity in the pure hydroxide solutions at higher concentrations. In Table V was shown $\gamma N/K = R$, where R is a constant. It would then be interesting to compare the values for the reaction velocities in pure hydroxide solutions on one side as calculated from the given activity coefficients of the alkali hydroxides and on the other as derived from the measurements at varying constant total molarity. Table VIII gives a summary of the calculations for potassium and sodium hydroxide solutions. To illustrate in a simple way the increasing speed of the reaction with rapidly growing alkali hydroxide concentration the half periods are given in seconds (T).

TABLE VIII
DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN SODIUM AND POTASSIUM
HYDROXIDE SOLUTIONS AT HIGH CONCENTRATIONS

A. Potassium Hydroxide Solutions					
N	γK from activity		γK from constant molarity		T
	γ_{MeOH}	K calcd.	$\log K/N$	K calcd.	
2.0	0.882	(0.47)	-0.631	(0.47)	39
3.0	1.086	.86	-.558	.83	21
4.0	1.362	1.45	-.470	1.36	12
5.0	1.723	2.29	-.373 ^a	2.12	7.9
6.0	2.194	3.49	-.252 ^a	3.36	5.2
B. Sodium Hydroxide Solutions					
2.0	0.732	(0.41)	-0.686	(0.41)	44
3.0	.840	.69	-.646	.68	26
4.0	.982	1.09	-.580	1.05	17
5.0	1.162	1.61	-.505	1.57	11
6.0	1.387	2.30	-.418	2.29	7.9

^a These values derived from measurements on potassium bromide solutions.

The values obtained by the two different methods for the decomposition velocity of diacetone alcohol in a hydroxide solution of a given concentration agree very well. This seems to indicate that the measurements on which these calculations are based must be consistent and have a fairly high degree of accuracy. It does not, however, exclude the possibility of certain systematic errors due to the experimental method used. The values calculated for hydroxide solutions with a higher concentration than 4 N are entirely hypothetical. There are a number of indications that these values may be approximately valid. It cannot be decided from the results given here whether the decomposition velocity with increasing hydroxide concentration finally reaches an upper limit which it does not exceed. If this were to be the case it seems that it should have been noticed long before this limit had been reached. Rather the contrary is observed, the reaction velocity accelerating with increasing hydroxide concentration.

To determine the decomposition velocity for lithium hydroxide solutions of higher concentrations than two, measurements were carried out with lithium chloride in 0.1 *N* hydroxide solutions. The solubility of lithium hydroxide decreases very rapidly with increasing lithium chloride concentration. Therefore no other measurements were made for salt solutions with higher hydroxide concentration than those given in Table VI. A summary of measurements and calculations is given in Table IX.

TABLE IX

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN LITHIUM HYDROXIDE SOLUTIONS AT VERY HIGH CONCENTRATIONS

$\frac{K}{N}$	$\frac{K}{N}$	$K \times 10^4$	$\frac{K}{N}$	$K \times 10^4$	$\log K/N$	N	$\log K/N$	K
0.1	0.5	158
.1	1.0	136	0.9	140*	-0.854
.1	1.5	118
.1	2.0	103	1.9	105*	-0.979	2.0	-0.762	(0.35)
.1	3.0	86.3	2.9	86*	-1.065	3.0	-.716	.58
.1	4.0	70.5	3.9	71*	-1.149	4.0	-.680	.84
.1	5.0	56.9	4.9	58*	-1.237	5.0	-.649	1.12
.1	6.0	46.9	5.9	47*	-1.328	6.0	-.621	(1.42)

* Interpolated values for the 0.1 *N* hydroxide solutions.

The velocity constants for concentrated, pure lithium hydroxide solutions calculated from the activity coefficients measured by Harned and Swindells agree fairly well with the values in Table IX. The agreement is, however, not as good as shown for potassium and sodium hydroxide solutions.

In Fig. 5 were shown the curves for $\log K/N$ for the three alkali hydroxide-chloride solutions at the constant total molarity of two. The most striking feature of these lines is that they seem to be very nearly parallel. If, instead of the alkali chlorides, the nitrates, bromides, iodides or thiocyanates had been used, apparently the same result would have been obtained. This is evident from a comparison with the velocity measurements given in the preceding paper and shown graphically in Fig. 10. The curves for the logarithm of the ratio between decomposition velocity and hydroxide concentration are given at the constant total molarity of 2 for potassium and sodium hydroxide solutions with the salts mentioned present. The curves for solutions where the salt present has the same anion seem to be parallel within the experimental errors. This also gives the reason why the velocity curves in various salt solutions with constant hydroxide concentration never cross each other, a point formerly stressed as important. With the constant total molarity curves for all salt hydroxide solutions of the same kind still assumed as straight, parallel lines different values would have been obtained for the velocity constant in a hydroxide solution of a given concentration if these curves crossed. This must, therefore, be impossible.

The activities of the chloride, bromide and iodide ions at the same concentration are probably quite different and the same must be true for the potassium, sodium and lithium ions. Still it was found that the direction of the curves in Fig. 5 was approximately independent

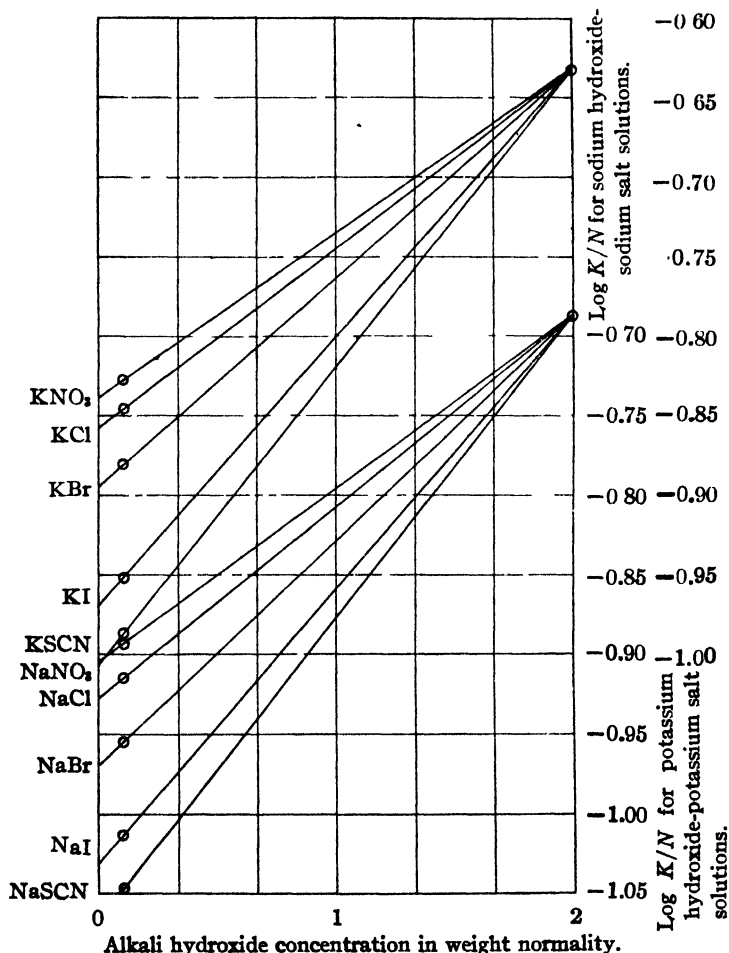


Fig. 10.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in alkali hydroxide-alkali salt solutions of constant total molarity with varying anion of the salt present.

of the nature of the cation and varied with the common anion of the salt present, which was shown in Fig. 10. Harned^{3a,b,2b} has given the following postulate for the activity coefficients of the ions of strong electrolytes. In solutions of strong electrolytes of the same valence type and with a common ion, at constant temperature and concentration, the activity

of this ion is a constant. In other words the logarithm of the activity coefficient of an ion is additive. At constant total molarity the concentration of the cation present is constant and thus its activity would be constant. This gives immediately the conclusion that the direction of the curves in Fig. 5 must be independent of the cation present, because when the activity of these ions is constant, then their influence on the reaction velocity may also be constant. The velocity changes would therefore be due solely to changes in the activity of the anions present. The halide ion may participate only indirectly in the reaction. The changes of the activity coefficient of the hydroxyl ion are then responsible for the variations of $\log K/N$ observed for potassium, sodium and lithium hydroxide-chloride solutions at constant total molarity.

VI. An Expression for the Reaction Velocity in Solutions with High Concentrations of the Electrolytes Present

Let us assume that we have an alkali hydroxide-alkali halide solution with only one salt present. The cation is common. At constant total molarity we have

$$\log \frac{K}{m_T - m_s} = B_s (m_T - m_s) + l \quad (1)$$

where m_T is the total concentration of the electrolytes present, m_s the salt concentration, B_s is a constant specific for the salt in the solution and l represents a function of the concentration. With decreasing salt concentration the following formulas are obtained for the pure hydroxide solution

$$\log \frac{K}{m_T} = B_s m_T + l \quad (2)$$

$$\frac{\gamma_{\text{MeOH}}(m_T) \cdot m_T}{K} = R \quad (3)$$

where R is a constant, which may be called the reduction factor between thermodynamic activity of the alkali hydroxide and reaction velocity. Substitution of l with Equations (2) and (3) gives for (1)

$$\log \frac{K}{m_T - m_s} = \log \gamma_{\text{MeOH}}(m_T) - \log R - B_s m_s \quad (4)$$

As mentioned before, $\log \gamma_{\text{MeOH}}$ may be expressed by the formula

$$\log \gamma_{\text{MeOH}} = - \frac{0.354 \sqrt{2m}}{1 + A \sqrt{2m}} + B 2m - \log (1 + 0.036 m) \quad (5)$$

where A and B are empirical constants. This gives finally

$$\log \frac{K \cdot R}{m_T - m_s} = - \frac{0.354 \sqrt{2m}}{1 + A \sqrt{2m}} + B 2m_T - \log (1 + 0.036 m_T) - \gamma m_s \quad (6)$$

It might be of some interest that Equation (6) is of the same type as the simplified form of the general equation deduced by Hückel¹¹ for the activity coefficient of a strong electrolyte. Harned and Åkerlöf have

¹¹ Hückel, *Physik. Z.*, **26**, 93 (1925).

shown that Hückel's general equation may be applied to the electromotive-force measurements for a large number of electrolytes in pure or mixed aqueous solutions. In Table X is given a comparison of observed reaction velocities and the values calculated from Equation (6). The observed values are interpolated from Table III in the preceding paper.

TABLE X

AGREEMENT BETWEEN OBSERVED REACTION VELOCITY AND THE VALUE CALCULATED FROM THE GENERAL EQUATION (6)

NaOH $A = 0.660$ $B = 0.050$		NaCl solutions $B_s = 0.117$ $(K \times 10^4)$		NaBr solutions $B_s = 0.139$ $(K \times 10^4)$		NaI solutions $B_s = 0.169$ $(K \times 10^4)$	
N	m_s	obs.	calcd.	obs.	calcd.	obs.	calcd.
0.1	0.9	152	146	146	139	134	131
.1	1.9	123	122	112	111	97	97
.1	2.9	102	106	93	92	74	75
.1	3.9	92	95	76	78	58	59
.1	4.9	84	86	63	67	46	48
.1	5.9	78	78	54	58	(39)	39

A better agreement between observed and calculated values could hardly be expected. It seems, however, as if the formula used might not be valid for solutions with small salt concentrations. It also cannot be used for hydroxide-salt solutions where the salt added increases the reaction velocity.

VII. Discussion

The measurements of relatively very high reaction velocities presented in this paper were not easy to carry out. The time required for every little detail had to be studied separately and shortened as far as possible or timed in such a way as to give the smallest possible error. The method is, therefore, not suitable for high precision measurements because it is too much hurried. It served to give fairly accurate and very important information in a so far completely unknown field. Its use might then be well justified. An attempt to work out an experimental method for measuring very high reaction velocities has been made by Hartridge and Roughton.¹² They give an excellent review of the theoretical possibilities and propose the use of rapidly flowing, continuously renewed solutions. For our purpose this would mean the use of very large quantities of highly concentrated alkali hydroxide solutions. A method using stationary solutions is, therefore, to be preferred if the desired sensitivity could be obtained.

In order to compare the results so far obtained from the study of the decomposition velocity of diacetone alcohol with results from investigations of other reactions, catalyzed by the same or other ions in solutions of strong electrolytes, we may first summarize the former.

¹² Hartridge and Roughton, *Proc. Roy. Soc. (London)*, **104A**, 376 (1923).

1. At constant alkali hydroxide and varying salt concentration all velocity curves had the same general form independent of the salt present. From the measurements at varying constant total molarity this was confirmed as a logical conclusion.

2. At constant total molarity $\log K/N$ varies linearly with the hydroxide concentration. At varying constant total molarity $\log K/N$ gives a number of parallel, straight lines.

3. The influence of the salt added is additive and thus also the slope of the constant total molarity curves is additive. With increasing activity of the salt the salt action in general increases.

4. In pure hydroxide solutions the velocity is proportional to the thermodynamic activity of the hydroxide present.

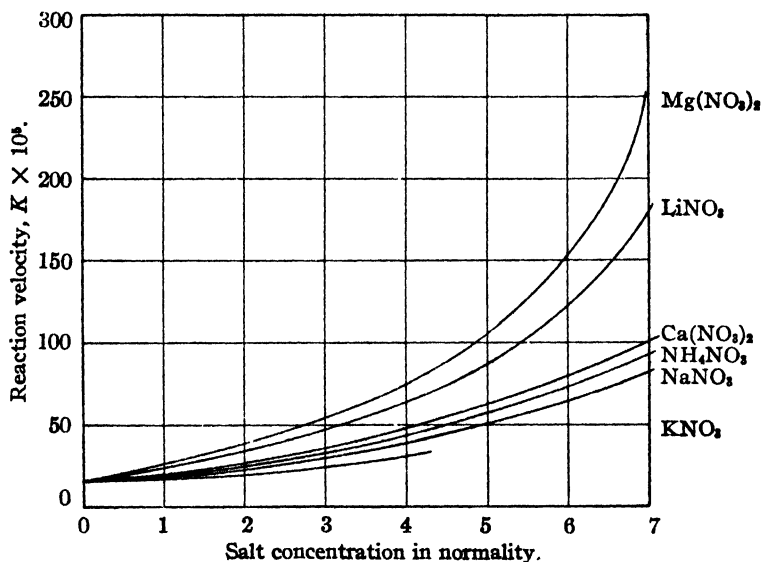


Fig. 11.—Curves for the velocity of hydrolysis of cyanamide in nitrate solutions of 0.25 *N* nitric acid.

Now we may compare these results with those for other reactions, and discuss what they have in common and where they differ. The first point seems to be valid for a large number of reactions. Harned¹³ and Åkerlöf¹⁴ have shown this for the hydrolysis of ethyl acetate, Grube and Schmid¹⁵ for the hydrolysis of cyanamide, Rivett¹⁶ for the conversion of acetylchloro-aminobenzene in acid-salt solutions. Harned¹³ found it to

¹³ Harned, *THIS JOURNAL*, **40**, 1461 (1918).

¹⁴ (a) Åkerlöf, *Medd. Vetenskapsakad. Nobelinst.*, **4**, 13 (1921); (b) *Z. physik. Chem.*, **98**, 260 (1921).

¹⁵ Grube and Schmid, *Z. physik. Chem.*, **119**, 19 (1926).

¹⁶ Rivett, *ibid.*, **82**, 201 (1913); **85**, 113 (1913).

be valid for the decomposition of hydrogen peroxide by the catalytic action of the iodine ion in salt solutions. A graphical demonstration may be obtained from Figs. 2, 3 and 4 in the preceding paper and Fig. 11 in this paper. We may, therefore, be justified in assuming this to approach the true conditions for all monomolecular reactions catalyzed by ions of strong electrolytes, as the halide acids, the alkali and alkali earth hydroxides and iodides. Exceptions to this rule are as yet unknown, but it might also be said that only a few cases have been studied.

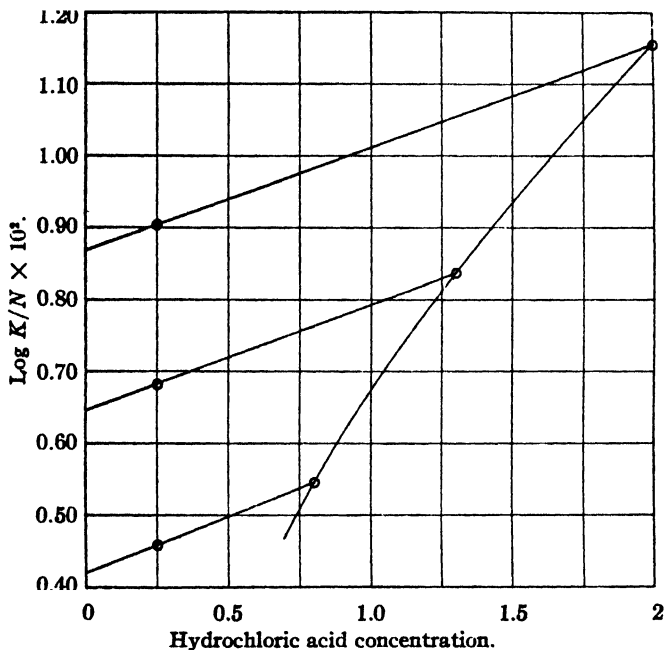


Fig. 12.—Curves for the logarithm of the ratio between conversion velocity of acetylchloro-aminobenzene and acid concentration in hydrochloric acid-sodium chloride solutions of varying constant total molarity.

The second point is far more difficult to investigate. In the literature there are no velocity measurements to be found for solutions with constant total molarity of the electrolytes present. However, this would not be any hindrance because the curves for varying constant total molarity were parallel. Thus, to study this case, only two points were necessary for each curve, one for a salt-catalyst, the other for the pure catalyst solution of the same total concentration. Measurements over a wider concentration range with solutions of the pure catalyst have seldom been carried out. Therefore a definite relationship between the thermodynamic properties of the catalyzing electrolyte and the reaction velocity generally

cannot be proved. Nor is it possible to make an extrapolation of the reaction velocity for solutions of high concentrations. Often the probable experimental errors seem to be quite large. With a very limited concentration range it must then be rather difficult to arrive at a safe decision from some of the material available.

In the literature there is one case to be found where all the requirements necessary for a study of this point over a short concentration range are fulfilled. Harned and Seltz measured the conversion of acetylchloro-aminobenzene to *p*-chloro-acetanilide in solutions of hydrochloric acid

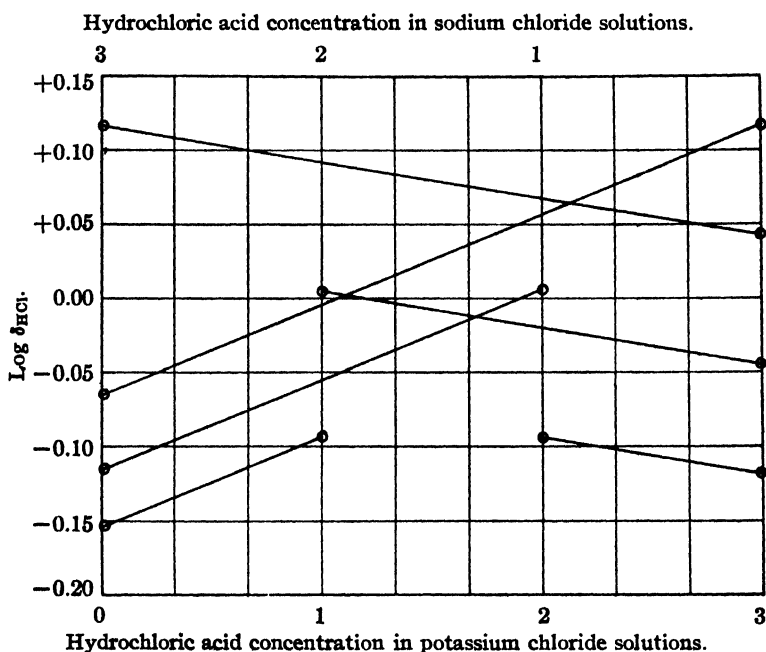


Fig. 13.—Curves for the logarithm of the activity coefficient of hydrochloric acid in potassium and sodium chloride solutions of varying constant total molarity.

up to a concentration of 1.0 *M*. They found a definite relation between activity of the acid and the reaction velocity

$$K = R\gamma_{\text{HCl}}^2 \cdot n_{\text{HCl}}^2 \quad (7)$$

where *R* is the reduction factor between reaction velocity and activity of the acid. The activity coefficient of hydrochloric acid may be given by an equation similar to (5).^{17,2a,b} In order to get the equation for the reaction velocity in acid-salt solutions, the measurements of Rivett for sodium chloride solutions in 0.25 *N* hydrochloric acid were interpolated. A few values of $\log K/N$ were plotted with these values for the pure

¹⁷ Scatchard, *THIS JOURNAL*, 47, 648 (1925).

acid solutions of the corresponding total concentrations. The curves obtained are given in Fig. 12. They must apparently be parallel, straight lines in analogy with the corresponding curves for the logarithm of the activity coefficient of hydrochloric acid in salt solutions at varying constant total molarity, which is shown graphically in Fig. 13 from the calculations of Harned and Åkerlöf. In regard to the calculations for the acetylchloro-aminobenzene reaction it may be noted that the concentration of the chlorine ion is constant at constant total molarity. Therefore $\log K$ is divided by the first power of the concentration of the acid, although the chlorine ion may participate in the catalysis.

In analogy with Equation (6) for the decomposition of diacetone alcohol, we, therefore, obtain the following formula for the conversion velocity in solutions with arbitrary acid-salt concentrations:

$$\log \frac{K \cdot R}{m_T - m_a} = -2 \left[\frac{0.354 \sqrt{2m_T}}{1 + A \sqrt{2m_T}} + B 2m_T + \log m_T - \log (1 + 0.036 m_T) \right] - B_s m_s \quad (8)$$

where B_s is a constant characteristic for the salt present in the solution. In Table XI is given a comparison of observed and calculated reaction velocities. The observed values are interpolated from the measurements of Rivett.

TABLE XI

AGREEMENT BETWEEN OBSERVED REACTION VELOCITIES AND THE VALUES CALCULATED FROM THE GENERAL EQUATION (8)

HCl $R = 13.8$ $A = 0.784$ $B = 0.0805$			KCl solutions $B_s = 0.181$ $K \times 10^4$		NaCl solutions $B_s = 0.162$ $K \times 10^4$		LiCl solutions $B_s = 0.107$ $K \times 10^4$	
m_T	$\gamma_{\text{HCl}}(m_T)$	m_s	obs.	calcd.	obs.	calcd.	obs.	calcd.
0.45	0.746	0.20	41.6	41.8	43.0	42.2	43.8	43.2
.65	.761	.40	58.2	57.8	60.7	59.0	63.1	62.0
.85	.786	.60	75.0	74.2	78.1	76.3	83.4	82.3
1.05	.818	.80	92.6	91.3	96.6	94.6	106	105
1.25	.855	1.00	111	110	116	114	129	130
1.45	.898	1.20	129	129	136	136	158	158
1.65	.944	1.40	148	149	157	159

The agreement between observed and calculated reaction velocity is very good. We have thus been able to show that also for the conversion of acetylchloro-aminobenzene the curves for $\log K/N$ at varying constant total molarity are represented by straight, parallel lines.

In the literature there are to be found measurements for two other reactions where this test could be applied as an indication that the reaction velocity is an activity function. These two reactions are the hydrolysis of ethyl acetate measured by Harned, Åkerlöf, Harned and Pfanstiel¹⁸ and others and the hydrolysis of cyanamide, measured by Grube and Schmid. For neither of these two reactions has been found a definite

¹⁸ Harned and Pfanstiel, *THIS JOURNAL*, **44**, 2193 (1922).

relationship between activity of the catalyst and reaction velocity. However, Harned and Pfanstiel have shown it to be very probable that the velocity of hydrolysis for ethyl acetate may be proportional to the activity

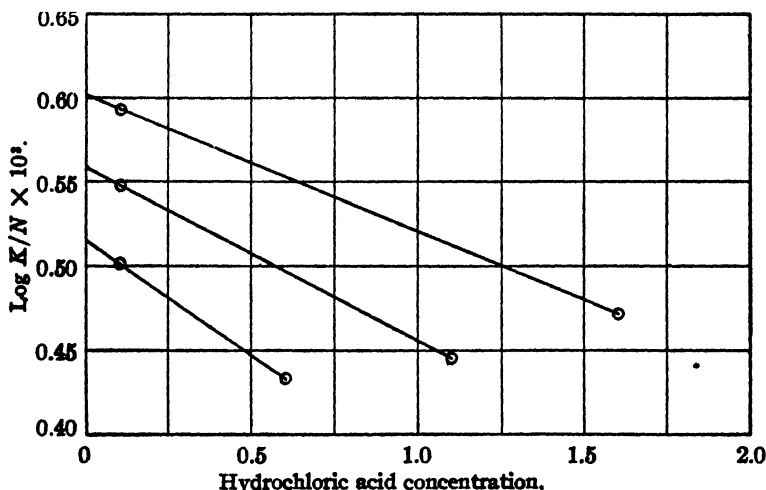


Fig. 14.—Curves for the logarithm of the ratio between velocity of hydrolysis for ethyl acetate and acid concentration in hydrochloric acid-sodium chloride solutions of varying constant total molarity.

of the hydrogen ion. The ratio between velocity and acid concentration shows a minimum at the same place as the individual activity coefficient of this ion. A graphical representation of the values for $\log K/N$ of

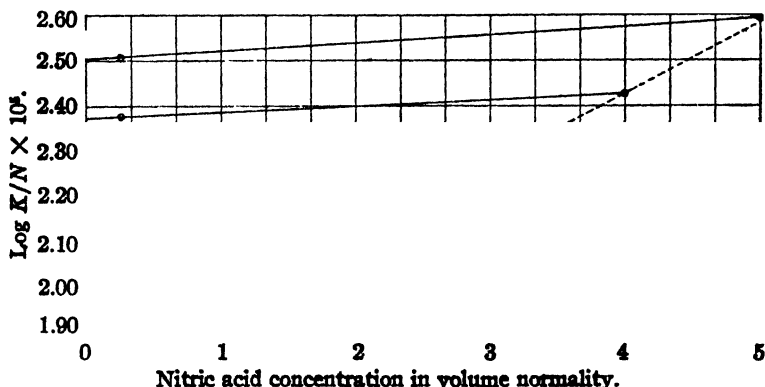


Fig. 15.—Curves for the logarithm of the velocity of hydrolysis for cyanide in nitric acid-lithium nitrate solutions of varying constant total molarity.

these two reactions in acid-salt solutions at varying constant total molarity is shown in Figs. 14 and 15. The data used for these figures, together with those for Fig. 12, are given in Table XII.

TABLE XII

DATA FOR FIGS. 12, 14 AND 15

I. Conversion of Acetylchloro-aminobenzene
Measurements of Harned and Seltz and Rivett

HCl m	NaCl m _s	K × 10 ⁴	Log K/m × 10 ³	HCl m	K × 10 ⁴	Log K/m × 10 ³
0.25	0.55	72.0	0.459	0.8	280	0.544
.25	1.05	120	.681	1.3	896	.838
.25	1.75	200	.903	2.0	2860	1.155

II. Hydrolysis of Ethyl Acetate

Measurements of Harned and of Harned and Pfanstiel

HCl m	NaCl m _s	K × 10 ⁴	Log K/m × 10 ³	HCl m	K × 10 ⁴	Log K/m × 10 ³
0.1	0.5	31.7	0.501	0.6	163	0.434
.1	1.0	35.3	.548	1.1	307	.446
.1	1.5	39.3	.594	1.6	474	.471

III. Hydrolysis of Cyanamide

Measurements of Grube and Schmid

HNO ₃ m	LiNO ₃ m _s	K × 10 ³	Log K/m × 10 ⁴	HNO ₃ m	K × 10 ³	Log K/m × 10 ⁴
0.25	0.75	21.8	1.941	1.0	91.7	1.962
.25	1.75	30.5	2.086	2.0	262	2.117
.25	2.75	42.7	2.232	3.0	555	2.267
.25	3.75	59.3	2.375	4.0	1065	2.425
.25	4.75	80.6	2.508	5.0	1950	2.591

The curves in Fig. 14 for the hydrolysis of ethyl acetate in hydrochloric acid-sodium chloride solutions appear to be only roughly parallel, with deviations in slope of about 5%. Certain facts may seem to indicate that these deviations could be within the experimental errors. Therefore we cannot safely decide whether these curves should be regarded as parallel or not. The curves in Fig. 15 represent a wide concentration range and they seem to be parallel within the experimental errors. The velocity of hydrolysis of cyanamide must, therefore, be regarded as a function of the activity of the electrolytes present.

Among other reactions where the velocity seems to be a function of the activity of the catalyst may be mentioned the inversion of cane sugar, although the data available are insufficient for a complete test. This reaction has been the subject for a very large number of small investigations. Each time only a few measurements were carried out. The sugar concentration used was usually rather high and varied considerably from one case to another. Therefore the measurements from different investigations cannot easily be compared with each other. However, Hantzsch and Weissberger¹⁹ have shown that the ratio between inversion velocity and acid concentration is greatest for the acid with the highest activity coefficient.

¹⁹ Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

For the decomposition of diacetone alcohol in alkali hydroxide-salt solutions the influence of the salt added upon the reaction velocity was found to be additive. In these solutions almost any kind of an alkali salt could be used for a study of this point. In acid solutions the number of suitable salts is quite limited. Salts of acids which must be regarded as weak electrolytes cannot be used for this purpose and the same is true for bi- and polyvalent acids. It seems as though in this case the differences between reaction velocities in alkali and alkali earth chloride and bromide solutions of their respective acids should be the simplest and easiest to measure. There are, however, no measurements to be found in the literature for a study of a possible additivity of the salt action on other reactions. It seems to be very probable that this might be the case, because the salt action is in general proportional to the activity of the salt added.

In our discussion a first attempt has been made to trace a general formula that may be used to express the velocity changes of simple reactions in catalyst-salt solutions as a function of the thermodynamic activities of the electrolytes present. It may perhaps be possible to use such an equation for a discussion of the intrinsic mechanism of these reactions. A large literature has grown up on this subject but positive, general results have seldom been attained. We were able to show that there seem to be other factors as yet unknown, but which must be known before we can arrive at a clear understanding of these processes.

VIII. Summary

In this paper are described measurements of reaction velocities with half periods down to thirty seconds. Attempts to measure still higher velocities were made and were partly successful. The values obtained were probably too low due to increasing, unpreventable, systematic errors.

With the method given, the decomposition velocity of diacetone alcohol has been measured in pure aqueous solutions of potassium, sodium and lithium hydroxide up to a concentration of 2.2 *N*. The velocity was found to be proportional to the activity of the hydroxide present.

Velocity measurements were then carried out for alkali chloride-hydroxide solutions with constant total molarity of 2. Log K/N varied linearly as a function of the hydroxide concentration, which is analogous to the behavior of the logarithm for the activity coefficient of the hydroxide.

Measurements at varying constant total molarity gave a number of parallel lines, just as the curves for the logarithm of the activity coefficient of the hydroxides in the same solution are straight, parallel lines. These lines extended to zero salt concentration gave the velocity in hydroxide solutions at high concentrations. Values obtained from the activity function agreed very well.

At all concentrations, even in very dilute solutions, it seems to be valid that the decomposition velocity of diacetone alcohol is a function of the thermodynamic activities of the electrolytes present. A short discussion of the measurements for other reactions as compared with those presented in this paper is given.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BOTANY OF THE
UNIVERSITY OF WASHINGTON]

THE ACIDITY OF THE WATERS OF SOME PUGET SOUND BOGS¹

BY THOMAS G. THOMPSON, JAMES R. LORAH AND GEORGE B. RIGG

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Introduction

This investigation was undertaken in order to ascertain the degree of acidity of certain bog waters and to study the relation of such acidity to the carbon dioxide content of the water, the color of the water and the stage of plant succession. It was thought that such data would be useful for interpreting the physiology of plants characteristic of bogs and also for explaining the rather marked corrosive action of such waters upon concrete and cement products.

Experimental

The waters studied were collected from four typical Puget Sound bogs. Two of the bogs, Esperance and Sunnydale, were characterized by the presence of methane dissolved in the waters and by the occurrence of a small pond which each bog surrounded. Bogs of this type have been designated as "wet bogs." The other two bogs, Ronald and White Center, experience a very great lowering of the water table in the summer months, evolve no methane and do not surround open bodies of water. Such bogs have been termed "dry bogs." A more detailed description of these bogs, their flora and the nature of the dissolved gases has been previously published.²

Effect of Dissolved Carbon Dioxide Upon Acidity

Samples of water were collected from at least two different points in each bog and the amounts of dissolved carbon dioxide carefully determined. This was accomplished by the complete removal of the dissolved gases by boiling the samples under diminished pressure for an hour.² Analyses of the liberated gases followed. Owing to the high dilution it was assumed that all of the carbon dioxide was present in the waters as carbonic acid,

¹ Read before the Chemical Section of the Pacific Division of the American Association for the Advancement of Science, June, 1927.

² *Bot. Gaz.*, 84, 264-278 (1927).

and from the primary ionization constant of the acid the hydrogen-ion concentration as P_H was calculated from the following

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = K = 3 \times 10^{-7}$$

$$P_H = \log 1/(H^+)$$

In Table I are given the parts per million of dissolved carbon dioxide in the different waters, the molality of such solutions and the calculated P_H . The calculations are given in the fourth column of the table and represent the maximum possible acidity due to the presence of carbonic acid.

TABLE I

THE CONCENTRATIONS OF CARBON DIOXIDE DISSOLVED IN THE WATERS OF THE DIFFERENT BOGS AND THE CALCULATED ACIDITIES PRODUCED BY THE PRESENCE OF THE GAS

Name of bog	Carbon dioxide, p.p.m.	Molality	P_H , calcd.
Esperance			
Hole No. 1	76.9	0.00174	4.64
Hole No. 2	71.9	.00163	4.65
Hole No. 3	68.3	.00155	4.67
Sunnydale			
Hole No. 1	71.6	.00163	4.66
Hole No. 2	40.0	.00091	4.77
Ronald			
Hole No. 1	33.8	.00077	4.82
Hole No. 2	55.8	.00126	4.71
White Center			
Hole No. 1	36.3	.00083	4.80
Hole No. 2	32.4	.00074	4.83
Lake Esperance	12.3	.00028	5.04

Several investigators³ have explained the acidity of bog or moor water as due to carbonic acid. The data presented in Table I, in some cases, check remarkably with those reported by Endell and thus tend to support this view. However, some preliminary experiments, the results of which are given in Table II, show that the acidity of bog waters is also due to an acid or acids other than carbonic acid. In these experiments a sample of water was collected from Esperance Bog, one was taken from the pond in the bog and another was a sample secured a year previous from Ronald Bog, which had been allowed to stand in a tightly stoppered bottle in the laboratory during this period. The acidity, using two different indicators for each sample, was determined with a double wedge comparator. The P_H was then determined electrometrically but, by the time

³ (a) Endell, *J. prakt. Chem.*, **82**, 414-422 (1910); (b) Stremme, *Z. prakt. Geol.*, **16**, 122-128 (1908); (c) Cowles and Schwitalla, *Ecology*, **4**, 402-416 (1923).

equilibrium was reached with this method, all of the carbon dioxide had been driven from the solution by the passage of the hydrogen gas. From the data given in Table II it will be noted that in one instance the removal of carbon dioxide decreased the acidity, while in the others the acidity was slightly increased. Varying results were obtained with the different indicators and these results may be explained by differences in sensitivity, effect of the characteristic yellow color of all of the waters and possibly by a difference in the adsorption of the indicator by the colloidal material.

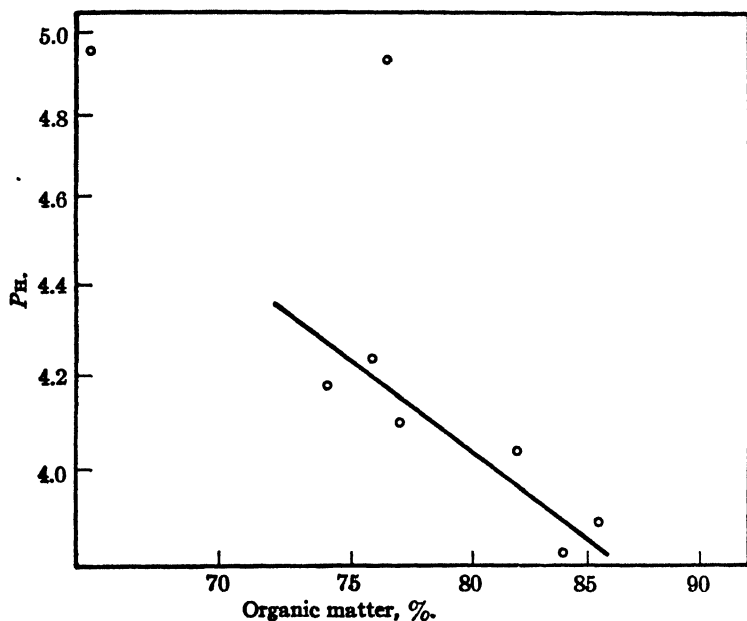


Fig. 1.—The relation between the acidity and the organic matter in bog waters.

A sample of water taken from a lake containing a small quantity of free carbonic acid showed a P_H of 6.3 with chlorophenol red, while the electrometric method gave a P_H of 7.95. The water of this lake had the characteristic yellow color of bog water and contained considerable quantities of colloidal matter. The carbon dioxide, in this particular case, produced the acidity and its removal caused a decrease past the neutral point. The colloidal material apparently had no effect upon the acidity. Much the same result was obtained with the water from Esperance Pond, except that the removal of the carbon dioxide did not produce an alkaline water. Comparing these data with those given for the bog waters, it is evident that the acidity of such bog waters is primarily due to an acid or acids in addition to the carbonic acid. The acid or acids are apparently stronger than the carbonic acid and the presence of the latter produces a buffering effect.

These observations are in accordance with those of Smorodinzew and

Adowa⁴ who noted a difference in the colorimetric and electrometric methods for the determination of the P_H of bog waters secured in the vicinity of Moscow. On thirty different samples their maximum plus variation was 0.71 with an average of 0.17. The maximum minus variation was 1.21 with an average of 0.46. The P_H of undiluted water from sphagnum measured electrometrically varied from 3.88 to 4.62, which is in accord with the measurements made on waters from bogs in the Puget Sound region as reported below.

To demonstrate still further that the acidity was due to acids other than carbonic acid, the experiments outlined in Table III were performed. In series No. 1 the sample of water was taken from the Sunnydale Bog, that in Series No. 2 represents the water from the pond in this bog, while those in Series 3 and 4 were taken from Esperance Bog, the sample used in Series No. 4 being secured from a hole dug very close to the pond.

All P_H determinations with the exception of some of those given in Table II were made by the ordinary method given by Clark⁵ with the use of a Leeds and Northrup potentiometer. The hydrogen electrodes were prepared from platinum foil and their accuracy was checked by buffer solutions. Because of the high resistance of some of the samples of water, the most sensitive type of wall galvanometer was utilized. Normal calomel electrodes, prepared from redistilled mercury, were employed and these were repeatedly checked against each other and also against electrodes used in other research work. The hydrogen was always passed through the water being tested and over the electrode for at least half an hour before readings were made.

TABLE II
COMPARISON OF COLORIMETRIC AND ELECTROMETRIC METHODS FOR THE DETERMINATION OF THE ACIDITY OF BOG WATERS

Source of sample	Electrometric P_H	Colorimetric P_H	Indicator
Esperance Bog	4.60	5.1	Chlorophenol red
		4.7	Bromocresol green
Ronald Bog	3.81	4.3	Bromophenol blue
		3.9	Bromocresol green
Esperance Pond	6.50	6.3	Chlorophenol red
		6.1	Bromothymol blue

Endell^{2a} in a study of the bogs of the Rhone region found that the colloidal material when separated by dialysis showed no acid reaction. If this is the case the acid substance is in true solution. Baumann and Gully,⁶ however, believe that the acid properties are due to colloidal properties, surface tension and adsorption by the cell membrane.

⁴ Smorodinzew and Adowa, *Arch. Hydrobiol.*, 17 (4), 673-677 (1926).

⁵ Clark, "The Determination of Hydrogen Ion," Williams and Wilkins, Baltimore, Md., 1923.

⁶ Baumann and Gully, *Mitt. Bayr. Moorkulturanst.*, 4, 31-156 (1910).

TABLE III

SERIES OF EXPERIMENTS WITH DIFFERENT WATERS DEVISED TO ILLUSTRATE THAT ACIDITY IS PRODUCED BY ACIDS OTHER THAN CARBONIC ACID

Series No. 1, P_H	Series No. 2, P_H	Manner of treatment of samples
4.02	5.92	Original samples of bog water.
4.03	5.88	After boiling for 5 minutes, cooling to original temperature and replacing the evaporated water with freshly boiled distilled water.
4.63	6.08	Dilution to twice the original volume with freshly boiled distilled water.
3.86	5.49	Concentration to 0.5 of original volume and cooling to original temperature.
3.56		Concentration to 0.2 of original volume and cooling to original temperature.
Series No. 3, P_H	Series No. 4, P_H	
4.30	4.92	Original samples of bog water.
4.29	4.83	After evaporating a definite volume to dryness at 90°, redissolving in freshly boiled distilled water and making up to original volume.

From the data presented in Table III the following facts are evident.

- (1) The P_H is the same after the sample has been boiled as it was before. The passage of hydrogen through the samples of the water lowered the partial pressure of the carbon dioxide to such an extent that it was completely expelled from solution and heating of the sample produced no further changes in acidity.
- (2) The acid substance is not appreciably volatile and is not affected by temperature changes.
- (3) The acid either forms a true solution in water and is very soluble or else it is a reversible colloid.
- (4) The change in acidity upon dilution and concentration is very similar to that which occurs with an acid buffered by a small amount of one of its salts.

Relation of Color to Acidity

The water of all four bogs studied, together with that of Lake Esperance, varied in color from a light yellow to a deep yellow. The intensity of the color was measured with a Lovibond tintometer, using yellow glass standards. The results are shown in Table IV. The samples were collected from two different places in four different bogs on February 27, 1926.

There appears to be rather an indefinite relation between color and acidity. The intensity of the color seems to increase with acidity. The later the stage of plant succession, the greater will be the color.

Acidity of Bog Waters

In Table V, is given the acidity of waters, collected over a period of fifteen months, from four different bogs. These samples were taken a month or so after the rainy season had started and in February, at the

TABLE IV
THE RELATION OF COLOR TO ACIDITY

Name of bog	Acidity, P_H	Water as collected	
		Observer, J. R. L.	Observer, K. W.
Ronald	3.83	2.00	2.00
	3.89	1.875	1.625
Sunnydale	4.23	1.50	
	4.04	1.50	1.50
White Center	4.17	1.125	1.25
	4.09	1.50	1.50
Esperance ^a	4.93	0.625	0.625
Lake Esperance ^a	4.95	1.125	1.125

^aAt the time these samples were taken the bog was flooded and much water drained from the bog into the lake and water from surrounding country drained into the bog.

height of the season. It was practically impossible to secure samples during the dry season owing to the marked lowering of the water table in

TABLE V
THE ACIDITY OF DIFFERENT BOG WATERS UNDER VARIOUS CONDITIONS

Sample no.	Date collected	Name of bog	Acidity, P_H	Description of conditions
1	11-28-24	Ronald	3.85	Minute particles of sphagnum suspended in sample. Determination run immediately after collection.
2	11-28-24	Ronald	3.85	Same as No. 1 but with all particles of sphagnum removed by filtration.
3	11-28-24	Ronald	4.11	A 2.5 liter bottle was filled with water used in No. 1. Thoroughly washed air was rapidly bubbled through the sample for forty-eight hours.
4	11-28-24	Ronald	3.83	2.5 liters of the water used in No. 1 was sealed in a bottle and kept for one year.
5	2-27-26	Ronald	3.83	Water from holes in two different portions of the bog taken at the height of the rainy season.
6	2-27-26	Ronald	3.89	
7	12-2-25	Sunnydale	4.40	35 feet from the pond in the bog.
8	2-27-26	Sunnydale	4.23	100 feet from the pond in the bog.
9	2-27-26	Sunnydale	4.04	150 feet from the pond where the conditions were much drier and the bog in a late stage of succession.
10	11-25-25	White Center	4.16	60 feet from marginal ditch.
11	12- 2-25	White Center	4.02	Center of bog.
12	2-27-26	White Center	4.09	200 feet from marginal ditch.
13	2-27-26	White Center	4.17	Center of bog.
14	11-25-26	Esperance	4.60	20 feet from the pond.
15	2-27-26	Esperance	4.93	30 feet from the pond. The entire bog was flooded.
16	10-31-25	Esperance	6.50	Water taken from pond.
17	2-27-26	Esperance	4.95	Water taken from pond. The entire bog was flooded.

the bog. The time at which the samples were collected appears to be of no consequence. The dominating factor influencing the degree of acidity is evidently the stage of succession of the bog, the acidity being directly proportional to the stage of succession.

It is a well known fact that aeration practically eliminates the toxicity of bogs to plant life. This is apparently due to two factors: (1) the removal of carbonic acid and the introduction of dissolved oxygen; (2) the partial oxidation of the organic material either chemically or by means of bacteria.

Sample 3 in Table V originally had a P_H of 3.85, but after thoroughly washed air had been passed through it continuously for forty-eight hours its acidity was decreased. The air was washed by first bubbling it through several bottles containing the bog water. This decrease in acidity indicates a partial oxidation of the acid-producing substance.

The acidities of the waters shown in Table V were all determined electrometrically and were not due to the presence of carbonic acid. In Table I is given the maximum acidity that might be expected from the presence of carbon dioxide.

The "dry" bogs, those containing no open water, have a greater acidity than the "wet" bogs. Furthermore, the acidity of the dry bogs is more constant than that of the wet bogs. The stage of succession and the drainage toward the pond, in the case of wet bogs, appear to be the dominating factors affecting the acidity.

In Table VI are given the results of the analyses of the different waters taken the same day from the four bogs. Two samples were taken at different places in each bog. In the third, fourth and fifth columns are given, as parts per million, the total solids, the ash and the organic matter. There appears to be a very definite relationship between the per cent. of organic matter and the acidity as expressed by

$$\% \text{ O. M. } \times P_H = K$$

This relationship is illustrated in Fig. 1.

TABLE VI
ANALYSES OF THE DIFFERENT BOG WATERS AND THE RELATION OF THE ORGANIC
MATTER TO P_H

Sample no.	Acidity, P_H	Total solids, p. p. m.	Ash, p. p. m.	Organic matter		$P_H \times$ per cent. O. M.
				p. p. m.	Per cent.	
5	3.83	88.6	14.6	74.0	83.52	3.20
6	3.89	89.1	13.1	76.0	85.30	3.32
8	4.23	77.2	18.8	58.4	75.65	3.20
9	4.04	82.7	15.2	67.5	81.62	3.30
12	4.09	45.2	10.4	34.8	76.99	3.15
13	4.17	83.9	21.8	62.1	74.01	3.09
15	4.93	54.7	12.9	41.8	76.41	3.77
17	4.95	75.8	26.2	49.6	65.43	3.24

Summary

1. While the acidity of bog waters of the Puget sound region may be due to carbonic acid, it is not the dominating cause of the acidity.
2. The maximum acidity that could be produced by carbonic acid is much less than that actually observed.
3. Colorimetric and electrometric methods for the measurement of acidity gave different results.
4. The acidity as measured electrometrically is not appreciably altered by evaporation of the waters and their dilution to the original volume.
5. There appears to be rather an indefinite relationship between color intensity and acidity.
6. The stage of succession of the bogs is directly proportional to the acidity.
7. "Dry" bogs show a greater acidity than "wet" bogs.
8. The per cent. of organic matter in the four bogs studied is a logarithmic function of the acidity. The amount of the organic matter present thus appears to be the controlling factor of acidity.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

A MICRO METHOD FOR THE DETERMINATION OF SURFACE TENSION AND DENSITY

BY V. RICHARD DAMERELL

RECEIVED JUNE 13, 1927

PUBLISHED DECEMBER 10, 1927

Although several micro methods for the determination of surface tension¹ and density² are known, none of the apparatus employed in these is applicable to both determinations. The purpose of this article is the description of an exceedingly simple apparatus by which surface tension and density can be determined on amounts of liquid as low as one-tenth of a cubic centimeter, with a theoretical accuracy of from one part in 100 to one part in 300, depending on the liquid.

Apparatus.—A ten centimeter portion of 5 mm. soft glass tubing was heated to softness in a Bunsen burner with wing top attachment and quickly pulled to arm's length. By running a three centimeter column of water up and down the resulting capillary, an eight centimeter portion that had practically uniform bore was found, and a ten centimeter length was cut out so that the eight centimeter portion was on one end. This

¹ (a) Du Noüy, *J. Gen. Physiol.*, **1**, 521-524 (1919); (b) Kiplinger, *THIS JOURNAL*, **42**, 472-476 (1920); (c) Sugden, *J. Chem. Soc.*, **119**, 1483-1492 (1921); (d) Ferguson, *Proc. Phys. Soc. London*, **36**, 37-44 (1923); (e) Richards, Speyers and Carver, *THIS JOURNAL*, **46**, 1196-1207 (1924).

² (a) Wartenberg, *Ber.*, **42**, 1126-1131 (1909); (b) Wiedbrauck, *Z. anorg. allgem. Chem.*, **122**, 167-170 (1922); (c) Detre, *Deut. med. Wochschr.*, **49**, 985 (1923).

end was filed flat and the other end notched, so the correct end could be used in all determinations. The radius was determined in the usual way with mercury and was found to be .01650 cm. A larger capillary was pulled, with a bore such that the small tube slipped in snugly, without sticking. This tube, used as a jacket, was made seven centimeters long and sealed at one end. A third tube, five centimeters long and sealed at one end was next made, being large enough to fit loosely over the jacket. This was the holding tube, used in the determination of density, to prevent the hands from touching the rest of the apparatus.

Determination of Surface Tension.—The jacket and holding tube were not used in the determination of surface tension. A small tube, with a capacity of about one-half of a cubic centimeter and 0.7 cm. in diameter, was used to hold the sample. This tube was put in a small thermostat and the liquid kept just at room temperature. The capillary tube (held close to the top by the fingers to prevent transfer of heat to the liquid) was lowered as nearly vertical as possible, so that the end just made contact with the liquid, in this way approaching the maximum rise from below. When the liquid had stopped rising, the capillary was pulled up, laid horizontally on a millimeter rule and measured by the eye to 0.1 mm. Now the end of the tube was dipped far into the liquid and after it had stopped rising was brought to the surface, thus approaching the maximum rise from above. To come from below again, a little of the liquid was shaken out of the tube and the first procedure repeated. Eight or ten readings were taken and the average recorded.

Determination of Density.—An assay balance weighing to 0.00001 g. was used. The weight of the capillary tube plus the jacket was first determined. Then the capillary tube was dipped in the liquid and the length of the column was determined as before, except that the capillary was held by forceps instead of the fingers. As soon as the length of the column was determined, a stop watch was started, the time of weighing being taken into account in order to correct for evaporation. The capillary was put into the jacket, great care being taken that none of the liquid ran out as it was being inserted, and the apparatus was weighed again. In all these operations the hands were kept off the apparatus, although a little practice was necessary to do this successfully. As soon as the second weighing was made, the time that the stop watch had been running was observed. The apparatus was left right on the balance, and at the end of another equal period of time a third weighing was made. The difference between the second and third weights was added to the first determined weight of the liquid, the assumption being made that the same weight of liquid would evaporate during each period of time. Since radius was known, as well as the length of the liquid column, the density was readily determined.

Experimental Results

TABLE I
SURFACE TENSION MEASUREMENTS

Subs.	Temp., °C.	Surface tension, dynes/cm.	Interpolated values of other observers for same temp.	Observer
H ₂ O	21	72.4	72.6	Accepted
C ₆ H ₆	18.5	29.5	29.2	Accepted
CCl ₄	23	25.7	25.3	Ramsay and Shields
			25.9	Jaeger
			26.4	Richards and Carver
(C ₂ H ₅) ₂ O	22	16.8	16.5	Jaeger
			16.6	Brunner
			16.8	Richards and Carver
C ₆ H ₅ CH ₃	23	28.4	27.6	Volkman
			28.4	Jaeger
			28.1	Richards and Carver
C ₆ H ₅ NO ₂	20	42.4	41.9	Ramsay and Shields
			43.2	Morgen (corrected)
			42.4	Jaeger
C ₆ H ₅ NH ₂	19	43.9	43.1	Jaeger
			43.6	Renard and Guye
			43.9	Volkman

TABLE II
DENSITY MEASUREMENTS ($R = 0.01650$ cm.)

Subs.	Temp., °C.	Observed density	Correct density
H ₂ O	22.5	1.002	0.998
C ₆ H ₅ N(CH ₃) ₂	23	0.950	.952
C ₆ H ₅ CH ₃	23	.857	.864
CCl ₄	25	1.592	1.584
C ₆ H ₅ NO ₂	26	1.188	1.198

Discussion of Results.—No correction for meniscus was applied, since due to the small bore of the capillary (.01650 cm.) the error introduced was negligible compared to the accuracy of the method as a whole.

Blowing into the tube, to force the liquid out in getting checks on the maximum rise, was found to introduce a large error. Results were also inconsistent when the tube was not wet with the liquid before determining maximum rise.

No readings were taken at other than room temperature, since with the present technique it is difficult to regulate the temperature of the liquid in the capillary.

In preparing the jacket for the capillary in determining density it was found essential to have one that fitted snugly. Otherwise, liquids like benzene and carbon tetrachloride were found to evaporate too rapidly to weigh accurately, in spite of the correction.

Liquids having a higher vapor pressure than 100 millimeters at 20°, such as ether and carbon disulfide, did not give satisfactory results in the determination of density.

Summary

A micro method for the determination of surface tension and density has been described which requires not over one-tenth of a cubic centimeter of sample for both determinations, which uses the same apparatus (with the addition of a jacket) for the determination of density as for the determination of surface tension and has an accuracy of from one part in 100 to one part in 300, depending on the liquid.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

IMPROVED APPARATUS FOR THE REMOVAL OF DISSOLVED GASES FROM WATER¹

BY JAMES R. LORAH, K. T. WILLIAMS AND THOMAS G. THOMPSON

RECEIVED JUNE 22, 1927

PUBLISHED DECEMBER 10, 1927

Many different forms of apparatus for the removal of dissolved gases have been described in the literature. In general they consist of three types: those employing vacuum only,² which include numerous modifications of the Van Slyke apparatus,³ those employing heat only,⁴ and those employing both heat and vacuum.⁵

Those of the latter type will remove gases from water more completely than the first two, and so an apparatus was designed which combines the good features of the Van Slyke type with those of the apparatus described by Treadwell-Hall. This improved apparatus has been used by the authors with excellent success for the removal of gases dissolved in natural waters. It is adaptable to any size of system or amount of gas, provides means of making a sharp separation of water from gas, employs the minimum number of joints consistent with ease of manipulation and also provides a seal for each joint.

¹ Read before the Chemical Section of the Pacific Coast Division of the American Association for the Advancement of Science.

² (a) Frankland, *J. Chem. Soc.*, 6, 109 (1854); (b) Lothar Meyer, *Z. anal. Chem.*, 2, 237 (1863); (c) Jones, Yant and Buxton, Bureau of Mines Reports of Investigations, No. 2553, December, 1923.

³ (a) McClendon, *J. Biol. Chem.*, 30, 259 (1917); (b) Van Slyke, *ibid.*, 30, 347 (1917); (c) Van Slyke and Stadie, *ibid.*, 49, 3, 44 (1921); (d) Austin and others, *ibid.*, 54, 129 (1922); (e) Hall, *ibid.*, 55, 751 (1923).

⁴ (a) Bunsen, "Gasometrischen Methoden," 1st ed., 1857, p. 18; (b) Reichardt, *Z. anal. Chem.*, 11, 271 (1872); (c) Jacobsen, *Ann.*, 167, 12 (1873); (d) Buchanan and Dittmar, "Physics and Chemistry, Report on the Scientific Results of the Voyage of H. M. S. *Challenger*," Longmans and Co., or Macmillan Co., 1884, I, p. 141; (e) Pettersson, *Ber.*, 22, 1434 (1899); (f) Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1924, 5th ed., Vol. II, p. 634, Fig. 128.

⁵ (a) McLeod, *J. Chem. Soc.*, 7, 313 (1855); (b) Hamberg, *J. prakt. Chem.*, 141, 433 (1885); (c) Hoppe-Seyler, *Z. anal. Chem.*, 31, 367 (1892); (d) Richardson, *J. Soc. Chem. Ind.*, 29, 198T (1910); (e) *ibid.*, 38, 32T (1919); (f) Ref. 4 f, p. 631, Fig. 127.

This apparatus consists of two separate pieces, a modified gas pipet and a special condenser. The latter consists of a $\frac{5}{16}$ " glass tube bent as shown in the diagram (Fig. 1) and surrounded by a water jacket, C. Adjoining this is a large bulb, B, to take care of the expansion of the water sample contained in the bottle when the latter is warmed. The tube, J, on the

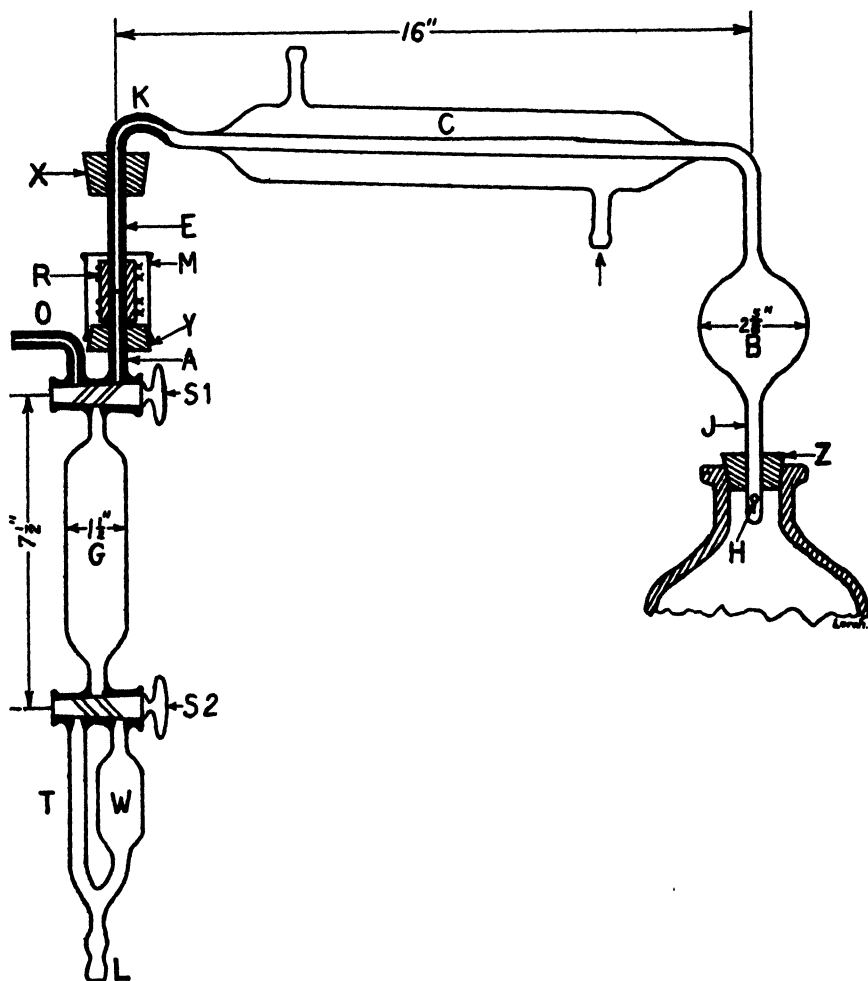


Fig. 1.

bulb, B, is sealed at the end and provided with a hole, H, about half an inch from the end. The opposite end, E, of the condenser tube is made of capillary tubing and is joined to the straight capillary tube, A, of the gas pipet by means of a short piece of heavy-walled rubber tubing, R. To provide a seal for this connection a large glass tube, M, is filled with mercury or water.

The gas pipet, G, is provided above and below with well-fitting stopcocks, preferably of the vacuum type. The upper stopcock, S1, leads to the condenser by means of the tube, A, and to a gas buret or storage pipet by means of the capillary outlet, O. The lower stopcock, S2, leads to the side tube, T, and to a small pipet, W, used for temporary storage of water. Both T and W open into L, to which a leveling bulb filled with mercury is attached. The entire apparatus is best made of Pyrex glass. The approximate dimensions are shown on the diagram, the capacity of B being about 200 cc., G, 100 cc. and W, 20 cc.

Since speed is essential in making the connections, the gas pipet and sample bottle of water must be arranged so that the ends of the condenser will fit with a minimum of readjustment. The condenser is sloped slightly so that the condensed water will run back into the bulb, B. The gas pipet is completely filled with mercury, including capillary tubes O and A.

The manipulation is as follows. Bulb, B, is filled two-thirds full with freshly boiled, distilled water by applying suction to the opposite end of the condenser tube and then stopper, Z, is moved down until it just covers hole, H. The condenser is held so that the water runs into the tube, J, and displaces all the air from it. The original stopper is now removed from the sample bottle and the neck of the latter carefully filled with freshly boiled, distilled water. This sample bottle, of course, has previously been placed in its correct position in the water-bath. Then stopper, Z, is inserted by pushing down on the bulb, B, with one hand and very slowly turning the stopper with the other, thus allowing a little water to be forced out of the bottle as the tube, J, is forced in. The latter is forced down until the top of the hole, H, just barely comes below the bottom of the stopper. As soon as the connection is made the height of the water in the water-bath is increased so that it forms a seal for this joint.

To remove all air from the condenser tube, bulb, B, is heated by a flame until almost all of the water has steamed away. During this operation no water is in the jacket, C, and the entire condenser must be turned horizontally to such an angle that no steam strikes the gas pipet. Then, with one person holding the condenser in position and continuing the heating of the bulb, B, with the flame, another person pushes the end, E, into the wetted rubber connection, R, while steam is still issuing from the end of the condenser tube. The rubber connection is immediately wired and the glass cylinder, M, lowered from stopper, X, to stopper, Y, and filled with water or mercury. While making connections the gas pipet should be protected from steam by means of toweling. Care should be taken to have the lower stopcock open to allow for possible expansion of mercury due to heating.

The sample of water is warmed to any desired temperature. If it is heated by applying external heat to the bottom of the bath it is best to

place blocks of wood under the bottom of the bottle to prevent superheating. A stirring device on the bath is very desirable.

Some water will expand from the sample bottle into the bulb, B. Any desired amount of vacuum may be produced by lowering the leveling bulb containing mercury attached to the bottom of the pipet at L. If any water accidentally enters the gas pipet, G, the mercury may be lowered until the water is drawn into the reservoir, W. Stopcock, S2, is then turned so that the by-pass, T, is open and the gas forced through, O, into a storage pipet or buret. Then the mercury is lowered until it reaches stopcock, S2, again, which is then turned so that as the mercury is raised again the water from W floats on top. It is carefully raised until the bend, K, is reached where the water flows back into the condenser tube. Before attempting this operation the collected gas already extracted must be removed as described.

After all gases have been removed from the sample, the water in bulb, B, is boiled for a couple of minutes to remove any gases present and then the stopper, Z, is loosened. By lowering the leveling bulb, the gas in the condenser tube and bulb is drawn over into the pipet, water entering the system through hole H. The bend, K, and the joint between the condenser tube and the capillary tube, E, enables one to make a clean separation of the gas and water. It was found that if a simple bend was used some gas always remained at the top of the bend.

Summary

A modification of the usual apparatus for removing dissolved gases in water has been described.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM RESEARCH DEPARTMENT, NATURAL PRODUCTS REFINING COMPANY]

A METHOD FOR DETERMINING THE TENSILE STRENGTH OF GELATIN JELLIES

BY A. ROSINGER AND J. J. VETTER

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PUBLISHED DECEMBER 10, 1927

Up to the present time the only scientific method for determining jelly strength has been by the use of the Sheppard torsion dynamometer.¹ This apparatus is used for testing the jelly strength of glues and gelatins by the pure shear of moulded cylindrical test pieces.

The following method, first suggested by A. Rosinger in 1923, depends on the static loading of jelly membranes, and is based on the fact that a circular elastic membrane supported rigidly at its circumference and subjected to air pressure on one side assumes a spherical form.

¹ (a) Sheppard and Sweet, *THIS JOURNAL*, 43, 539 (1921); (b) Sheppard, Sweet and Scott, *J. Ind. Eng. Chem.*, 12, 1007 (1920).

When the wall thickness d' of a spherical surface is small compared to the radius r of the sphere, and the pressure within is p , the tensile stress (see any textbook on strength of material)

$$\sigma = \frac{pr}{2d'} \quad (1)$$

If we know the radius a of the frame holding the jelly membrane—a constant for the apparatus—and the height h of the spherical segment, the radius r of the sphere is

$$r = \frac{a^2\pi h^2}{2h} \quad (2)$$

There is no change in volume when a gel undergoes extension,² therefore by measuring the original thickness d of the jelly membrane the actual thickness d' for any radius up to the breaking point can be determined from the equation

$$d' = \frac{a^2\pi d}{\pi(a^2 + h^2)} = \frac{a^2d}{a^2 + h^2} \quad (3)$$

By substituting the values of r and d' from Equations 2 and 3 in Equation 1, we obtain

$$p \frac{1}{4 a^2 d} \cdot \frac{(a^2 + h^2)^2}{h} \quad (4)$$

and letting

$$\frac{1}{4 a^2 d} = c \text{ and } \frac{(a^2 + h^2)^2}{h} = x$$

the tensile stress becomes

$$\sigma = cpx \quad (5)$$

The experimental data necessary for the determination of the tensile strength are

original membrane thickness	d
volume of spherical segment	V
pressure on membrane	p

The surface elongation is

$$E = \frac{\pi(a^2 + h^2) - \pi a^2}{\pi a^2} = \frac{h^2}{a^2} \quad (6)$$

and the linear elongation is

$$\epsilon = \frac{l' - l}{l} = \frac{\sqrt{\pi(a^2 + h^2)} - \sqrt{\pi a^2}}{\sqrt{\pi a^2}} \quad (7)$$

Fig. 1 shows V , ϵ and x as functions of h .

The value d may be conveniently measured with a microscope by attaching a scale to the adjusting screw and focusing on the upper and lower surfaces of the membrane, and the height h of the spherical segment may be obtained from the volume of the latter, instead of by direct measurement. See Fig. 1.

² Bogue, "Colloidal Behavior," McGraw-Hill Book Co., New York, 1924, Vol. 1, p. 412.

The apparatus, Fig. 2, consists of three parts: A, the bell for holding the membrane, fitted with a two-way stopcock; B, the buret with the manometer tube; and C, the reservoir for adjusting the total amount of air in the system to a definite volume.

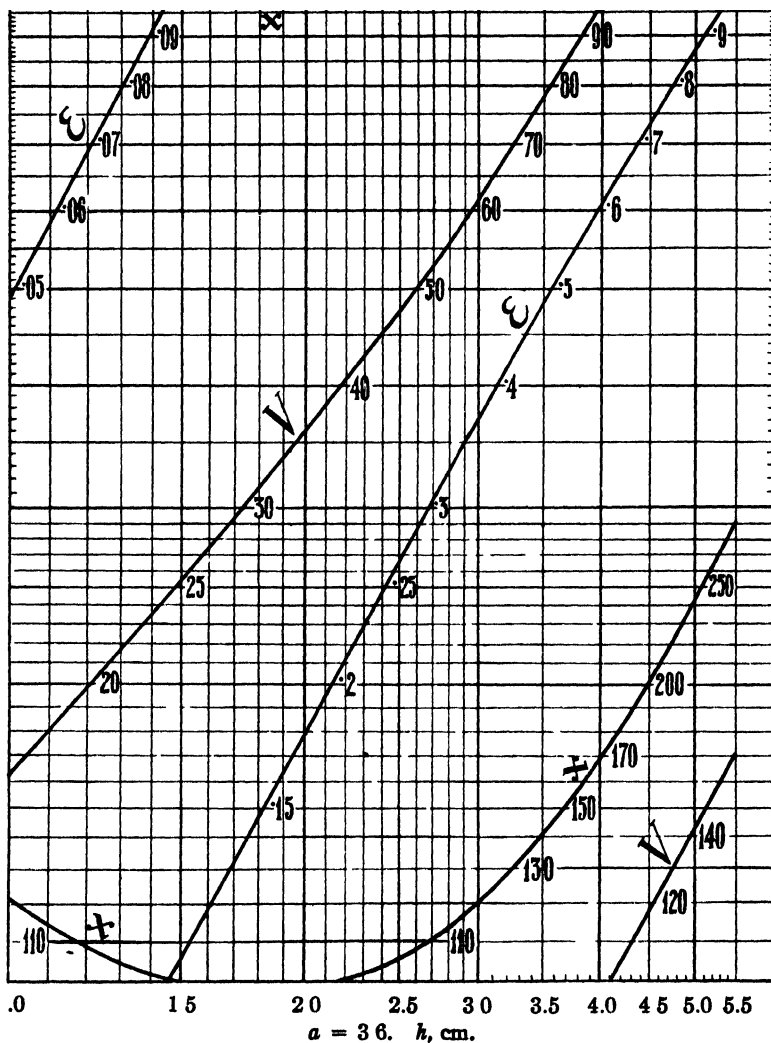


Fig. 1.

Experimental Part

The bell A is placed on a mercury surface and the gelatin solution poured in through the neck. After standing a definite time to set, the stopcock tube is attached to the bell and the latter shut off from the outside

air while being attached to the apparatus. The water level in C is adjusted to give a definite volume of air in the apparatus (1 liter) and water is run into the buret from a bottle above the apparatus to the zero point. The two-way stopcock attached to the bell is next turned to connect the latter with the apparatus and seal off the outside air. Water is run into

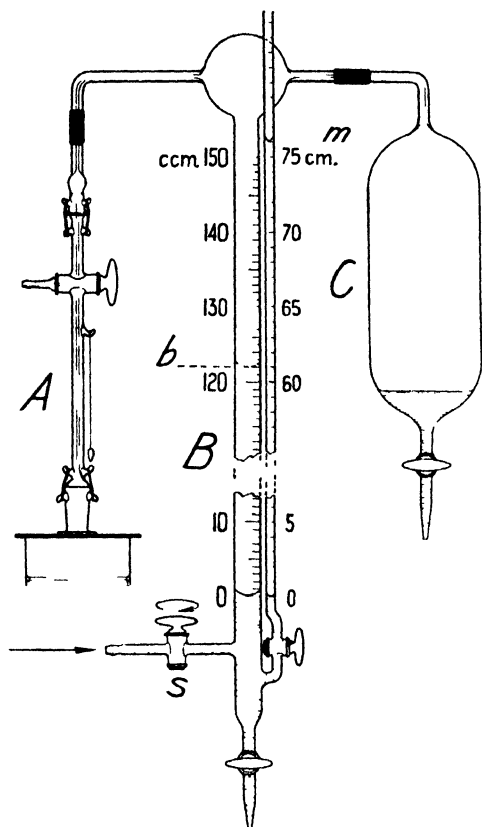


Fig. 2.

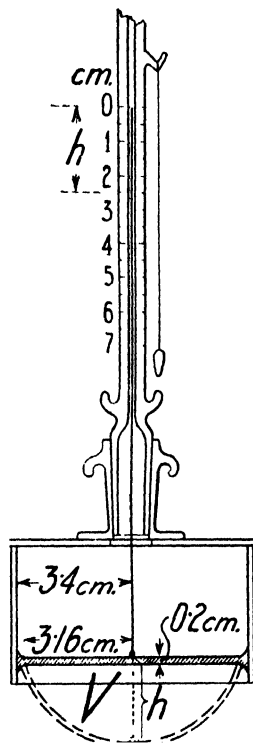


Fig. 3.

the buret through the stopcock S in 5cc. or 10cc. portions at a time and buret and manometer readings are taken after each addition. In releasing the pressure on the membrane, water is run out of the buret from the stopcock at the bottom in small portions at a time and buret and manometer readings are again taken. If a test is to be run over a considerable period of time, a beaker containing a small amount of water may be placed under the bell A to check evaporation from the membrane surface.

All membranes in the following tests were made from gelatin solutions prepared by soaking dry gelatin in cold water for fifteen minutes, heating

to 60° for five minutes and filtering. They were tested at 22 to 24° after standing for twenty hours.

To determine experimentally the value of a the arrangement shown in Fig. 3 was set up, using a very fine glass filament resting in the center

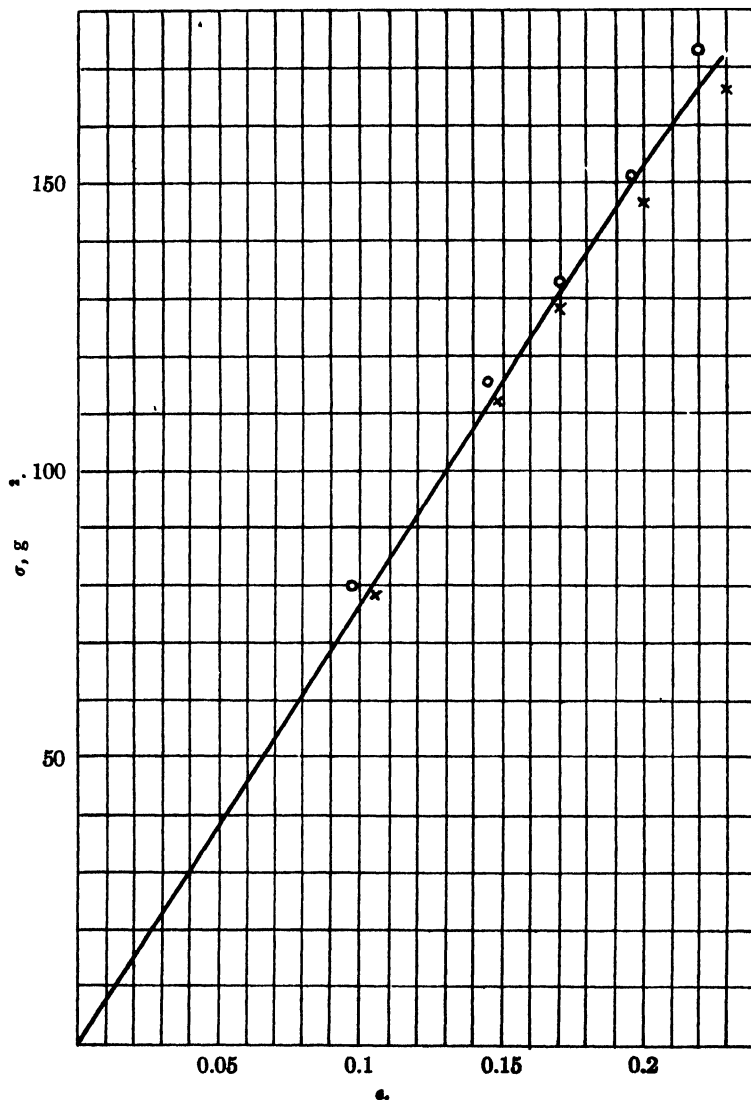


Fig. 4.

of the membrane and measuring the distance between the original and final positions in the graduated tube to find h , from which the value of a was calculated (see Table I).

TABLE I
DETERMINATION OF THE VALUE a

Eastman gelatin, P 1099; 20% jelly; 24 hours' setting; room temperature; $d = 0.2$

b	h , cm.	p , g./cm. ²	V , cc.	
0.0	0.0	0.0	0.0	
10.0	6.3	0.65	1.3	2.9
15.0	9.7	0.85	2.2	3.05
20.0	13.4	1.05	3.4	3.11
30.0	21.0	1.45	6.0	3.13
35.0	24.85	1.60	7.35	3.19
40.0	28.65	1.75	8.65	3.22
45.0	32.35	2.05	10.1	3.12

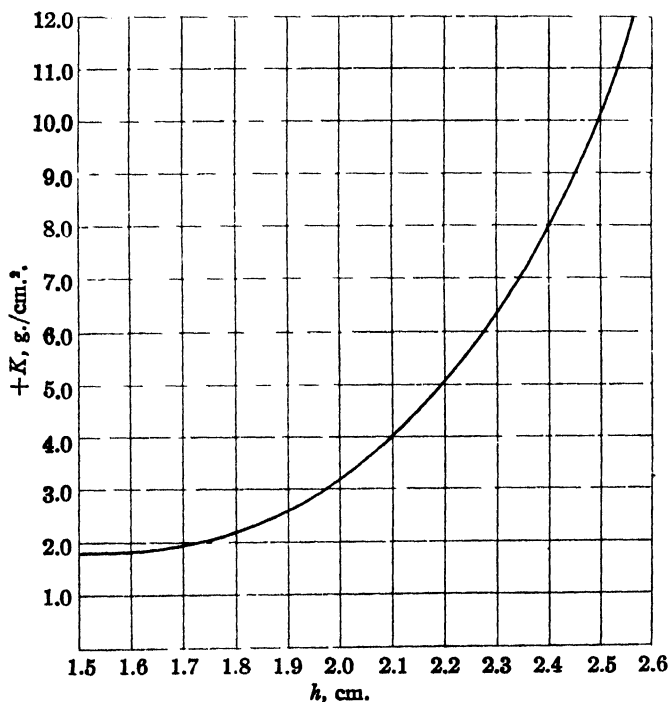
Av. 3.16

b = buret reading; m = manometer reading; buret cross section, 2 cm.²; $p =$

$m - b/2$; $V = b - p$; from the equation V

average, $a = 3.16$; $a^2 = 10$.

To determine the influence of gravity on the results, tests were made with duplicate samples, running one with the bell vertically upward



$d = 0.2$ cm.; 20% jelly, $\nu = 1.055$.

Fig. 5.

and the other downward. The result is shown in Table II and Fig. 4. The error due to gravity was eliminated by taking the mean of the two

curves. Fig. 5 shows the corrections to be made when the bell is held in a downward position with a membrane thickness of 0.2 cm. and gelatin

150 |

100

50

50

0.1

0.2

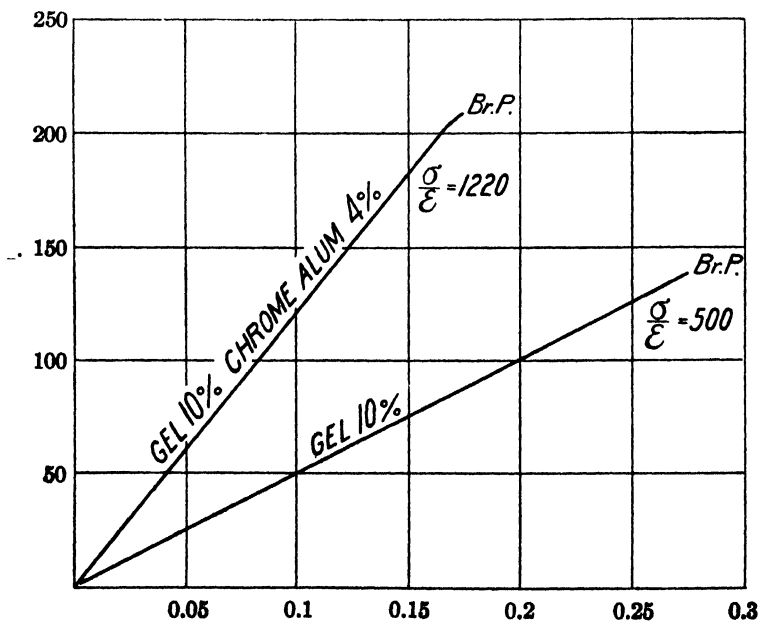
0.3

a.

Fig. 6.

concentration of 20%. The correction K_1 for membranes of thickness d and density δ is

$$K_1 = K \frac{\delta d}{1.055 \times 0.2} - K \frac{\delta d}{0.211} \quad (8)$$



a.

Fig. 7.

The value of a in the present experiments was determined for membranes from 0.2–0.3 cm. thick. For thicker or thinner membranes a new a value should be determined.

The following experiments showing the application of this method have been corrected for the effect of gravity.

Fig. 6 and Table III show the results of a test on "Silver Label" gelatin.

Fig. 7 shows the effect of chrome alum on the same gelatin.

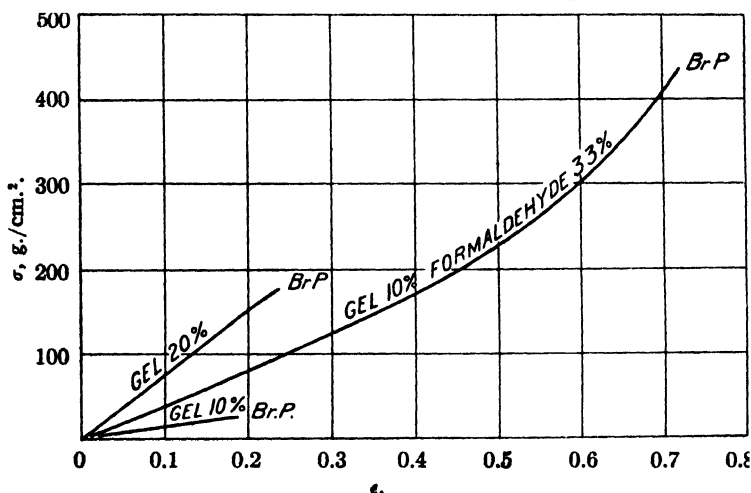


Fig. 8.

Fig. 8 shows the effect up to the breaking point, Br. P., of formaldehyde on Eastman gelatin P 1099. It is interesting to note that chrome alum does not change the character of the elasticity curve while formaldehyde produces a curve closely resembling rubber.

TABLE II
EFFECT OF GRAVITY

Eastman gelatin, P 1099; 20% jelly; twenty-four hours' setting; room temperature; $d = 0.2$ cm.; $c = 0.125$.

b	m	p , g./cm. ³	V , cc.	h , cm.	X		σ , g./cm. ²
30.0	21.3	6.3	23.7	1.5	100.0	0.105	78.75
40.0	29.2	9.2	30.8	1.825	97.5	.148	112.10
45.0	33.0	10.5	34.5	1.95	98.0	.170	128.65
50.0	36.8	11.8	38.2	2.15	99.5	.200	146.75
55.0	40.6	13.1	41.9	2.3	101.5	.230	166.2

Bell vertically downward.

30.0	21.6	6.6	23.4	1.45	101.0	0.098	80.0
40.0	29.5	9.5	30.5	1.8	97.5	.145	115.8
45.0	33.35	10.85	34.15	1.95	98.0	.170	133.0
50.0	37.2	12.2	37.8	2.1	99.0	.195	151.0
55.0	41.2	13.7	40.3	2.25	101.0	.220	173.0

Bell vertically upward.

TABLE III
TEST ON "SILVER LABEL" GELATIN

b	p , g./cm. ²	V , cc.	h , cm.	X	e	σ , g./cm. ²	$+K_1$	σ , g./cm. ² , corr.	
31.0	21.05	5.55	25.45	1.55	99.5	0.110	58.5	1.9	60.4
40.0	27.7	7.7	32.3	1.875	98.5	.157	80.4	1.9	82.3
44.0	30.65	8.65	35.35	2.025	98.0	.183	89.8	3.5	93.3
50.0	35.00	10.00	40.00	2.225	100.05	.215	106.05	5.7	111.75
55.0	38.60	11.10	43.9	2.4	103.5	.243	121.8	8.8	130.6
60.0	42.0	12.0	48.0	2.55	106.5	.275	127.8	12.1	139.9

Gelatin, "Silver Label;" % jelly; twenty hours' setting; room temperature;
0.235 cm.; $c = 0.106$; $\delta = .03$; $K_1 = 1.1$ K.

TABLE IV
DENSITY OF GELATIN JELLIES^a

Concn., %	Gelatin α	Sp. gr.	Concn., %	Gelatin β	Sp. gr.
5		1.014	5		1.014
10		1.028	10		1.030
20		1.054	20		.060
30		1.088	30		.094
40		1.122	40		.132
50		1.166	50		.172

^a P. Bary, "Les Colloides," Dunod, Paris, 1921, p. 42.

In calculating the tensile strength, the actual thickness of the membrane at the moment the readings are taken is used and not the original thickness, as in most previous work on this subject.

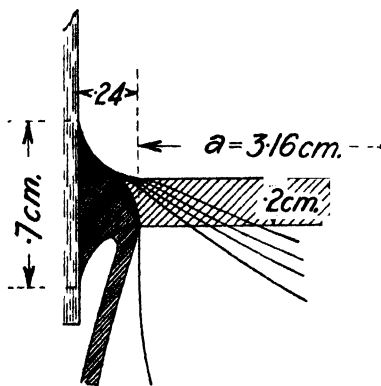


Fig. 9.

With the dimensions of the apparatus as given in Fig. 1, the volume of the inclosed air (one liter) can be considered to decrease 1 cc. for each cm. of pressure, p , within the pressure range used in the tests.

Fig. 9 shows the form taken by the membrane, when stretched, at the junction with the glass, and shows that the upper point to which h is measured or calculated from the inner surface of the membrane is not a fixed point but lowers slightly as h increases. When h is less than 3 cm. no correction need be made.

Summary

An apparatus and method for studying the elastic properties of gelatin jellies under static loading conditions are described.

The apparatus can be used to study the time of relaxation of stretched membranes.

The method is applicable to the study of any elastic medium that can be formed into a membrane.

The influence of chrome alum and formaldehyde on gelatin jellies is shown.

JERSEY CITY, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA
AT LOS ANGELES]

THE VAPOR PRESSURES OF POTASSIUM AMALGAMS

BY RUSSELL W. MILLAR

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According to the freezing point-composition curves of the amalgams of the alkali and alkaline earth metals,¹ these solutions should possess properties far different from those of the ideal solution. This assumption is confirmed by the vapor-pressure and electromotive-force measurements of several investigators.²

On account of the ease of distillation and availability of metallic potassium, its amalgams were chosen for study as examples of extremely imperfect solutions.

The method was that of Ramsay, which has been used by practically all investigators in this field. A closed J-tube was filled with the amalgam and thoroughly boiled out *in vacuo*, so that the short, closed arm contained no gas. The amalgam was then brought to a constant temperature and the pressure of the mercury vapor in the closed arm was balanced by that of hydrogen in the long arm. The pressure of the hydrogen was measured by means of a manometer. The fine adjustment of the hydrogen pressure was accomplished by means of a narrow barometric column as used by Hildebrand in his measurements of the vapor pressures of zinc amalgams.³

Apparatus.—The J-tube was of heavy-walled Pyrex tubing of 0.70 cm. internal diameter. The short arm was 3–4 cm. in length. The temperature was maintained by means of a well-insulated air-bath in which the temperature was kept uniform by means of a fan. Windows permitted observation of the amalgam. The voltage of the lighting circuit by which the oven was heated varied considerably, but it was found that equilibrium was attained so rapidly that the readings obtained fell upon the same curve whether the temperature was rising or falling.

The temperature was measured by means of a nichrome-constantan thermocouple

¹ (a) Jänecke, *Z. physik. Chem.*, **57**, 510 (1907). (b) Smits and Beck, *Proc. Acad. Sci. Amsterdam*, **23**, 975 (1921).

² (a) Ramsay, *J. Chem. Soc.*, **55**, 521 (1889). (b) Meyer, *Z. physik. Chem.*, **7**, 477 (1891). (c) Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). (d) von Wartenberg, *ibid.*, **20**, 443 (1914). (e) Eucken and Neumann, *ibid.*, **28**, 322 (1922). (f) Fay and North, *Am. Chem. J.*, **25**, 216 (1901). (g) Beckmann and Liesche, *Z. anorg. Chem.*, **89**, 171 (1914). (h) Beck, *Rec. trav. chim.*, **41**, 353 (1922).

³ Hildebrand, *Trans. Am. Electrochem. Soc.*, **32**, 319 (1913).

which was chosen because its e.m.f. varies almost linearly with the temperature and the coefficient is high. The e.m.f. was measured with a Leeds and Northrup "Type K" potentiometer and an unsaturated Weston standard cell which was checked against one calibrated by the Bureau of Standards. The thermocouple was calibrated against the boiling points of water and of naphthalene and the melting point of a sample of zinc furnished for the purpose by the Bureau of Standards. The e.m.f.'s observed were found to be represented accurately by the equation used by Eastman and Rodebush⁴ for copper-constantan at low temperatures

$$E = E_0 + aT^n$$

where E = e.m.f., and in the present instance $E_0 = -6840$, $\log a = 0.05706$, $n = 1.5490$ and T = degrees Kelvin. From this formula a table was constructed and all readings were converted to temperatures by its aid. The temperature scale was checked against that used by Smith and Menzies⁵ in their determination of the vapor pressure of pure

mercury by a similar determination with the apparatus used for the amalgams. The results are shown in Table I, which gives the pressures found and those calculated from the formula of Smith and Menzies. The divergence indicates the order of the experimental error; for instance, the temperature was known only to about 0.5° .

The pressure of the hydrogen was measured with a closed mercury manometer of 1.5 cm. internal diameter which was placed before an accurate steel scale. Readings were taken through a telescope placed about 2 meters distant.

Materials.—The mercury was washed three times by spraying through a column of dilute nitric acid 150 cm. high and twice distilled in a current of air under reduced pressure.

The amalgam was then made in a Pyrex glass apparatus represented by Fig. 1, which is one-third actual size. Having been well cleaned, the apparatus was first evacuated through the stopcock S by means of a mercury diffusion pump and heated almost to the softening point of the glass for about fifteen minutes. Air was then admitted, the tips of E and C were broken off and the desired amount of mercury was introduced through C, which was then sealed. The potassium, which had been kept under ether and dried beforehand, was placed in E, which was then sealed. The apparatus was evacuated for about two hours and strong heating of the parts which did not contain potassium or mercury was repeated at intervals. The potassium was warmed, but not melted, and the mercury was boiled gently. Finally, after a 500 cc. McLeod gage connected to the line showed not more than 0.00005 mm. pressure of mercury when the apparatus was hot, the potassium was melted. It ran readily through the capillary F into the first bulb D, leaving the oxide shell in E, which was then sealed off at F and discarded.⁶ The potassium was then distilled from one bulb D to the next and the residue in each case was sealed off. From the last bulb the potassium was distilled

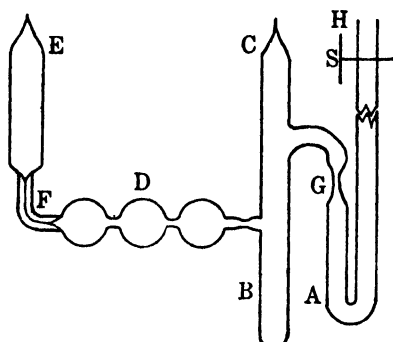


Fig. 1.

⁴ Eastman and Rodebush, *THIS JOURNAL*, 40, 499 (1918).

⁵ Smith and Menzies, *ibid.*, 32, 1434 (1910).

⁶ This method of cleaning the alkali metals was described by Lewis and Kraus, *THIS JOURNAL*, 32, 1459 (1910).

slowly into the mercury in B. The stopcock was then closed and the J-tube A with the stopcock and the attached tube B was broken off at H. The amalgam was then well mixed and the amount poured into A which was necessary to fill it from the point G slightly past the bend. The tube was then sealed to the vacuum line and B was sealed off at G. Hydrogen was next admitted. During all of these operations it was necessary to keep the tube and its contents warm in the cases of the more concentrated amalgams, for the frozen amalgams always broke the tube on melting. The three more dilute amalgams had the color of mercury, but the three more concentrated ones were gray to copper-colored. The remaining portions of the concentrated amalgams, which were examined in B, were fairly hard and of considerable mechanical strength. It is not thought that the color of the concentrated amalgams was due to impurity or to moisture in the glass, for it appeared as soon as the potassium and mercury came into contact and did not increase in the presence of hydrogen. Indeed, mercury vapor, which was always present near the top of B, turned the bright surface of the globules of potassium almost black.

The hydrogen was produced by the electrolysis of sodium hydroxide solution, passed over hot platinized asbestos and dried with phosphorus pentoxide. It had no visible effect upon the amalgams.

TABLE I
THE VAPOR PRESSURE OF MERCURY

T, °K.	$p_{\text{mm.}}$, obs.	Smith and Menzies
468.3	14.7	14.77
518.0	62.4	64.88
571.9	244.8	240.05
575.3	258.7	258.37
613.0	560.7	555.6
613.9	570.4	565.2

Analysis.—The tube containing the amalgam was sealed off, broken and dropped into an excess of 0.5000 *N* hydrochloric acid. A piece of platinum wire aided the solution of the metal, which was complete in about twelve hours. The excess of acid was then titrated and the mercury, after washing and drying at 40°, was weighed. Check results were obtained on the excess of amalgam remaining in B after the amount needed had been poured into A.

There were several sources of error on account of which the results can lay no claim to high accuracy. Even with pure mercury the error was about 2%, due largely to the leak of heat up the thermocouple leads. The use of a radiation shield around the thermocouple and the J-tube did not affect the readings except when it obscured the levels of the amalgam. The amalgams of low concentration did not affect the glass but those of the highest concentrations darkened it after a time and then showed a tendency to stick slightly.

Two serious sources of error were the evaporation of mercury into the open arm of the tube and the accumulation of hydrogen in the closed arm, the former causing low results, the latter high. The pressure of the hydro-

gen was removed frequently, so that the amalgam boiled into the open arm of the tube and at the same time the mercury which distilled and condensed on the upper part of the tube was shaken down by violent tapping. After this operation hydrogen could not be detected in the narrow tip at B where the tube had been sealed off and the mercury in the open arm was kept at a minimum. The tube, when taken for the analysis, was always drawn off at a point which had been inside of the furnace, so that mercury which had condensed in the open arm remained there. The errors in the steel scale and the reading of the manometer were less than those mentioned above.

TABLE II
VAPOR PRESSURES OF POTASSIUM AMALGAMS

No. 1, $N_2 = 0.0492$		No. 3, $N_2 = 0.0877$			
$T, ^\circ K.$	$p_{mm. \text{ of Hg}}$	$T, ^\circ K.$	$p_{mm. \text{ of Hg}}$	$T, ^\circ K.$	$p_{mm. \text{ of Hg}}$
516.5	54.3	457.2	7.4	558.6	65.3
516.9	55.4	457.2	7.8	578.5	101.2
590.8	319.8	457.8	8.0	579.4	103.2
591.6	331.2	459.5	8.2	579.8	104.4
593.1	339.3	461.8	9.0	580.0	104.6
601.7	402.7	482.0	16.7	580.5	106.0
603.3	416.6	483.6	18.1	643.4	377.7
606.8	456.0	484.4	18.4	644.9	387.5
608.0	458.4	490.6	22.0	648.0	407.8
		506.2	34.2	649.6	415.3
No. 2, $N_2 = 0.0552$		517.0	43.9	No. 5, $N_2 = 0.321$	
513.5	49.2	568.1	174.8	564.8	10.0
513.8	49.8	617.7	446.2	565.1	9.8
514.4	50.6	618.2	451.3	565.4	9.6
515.9	53.0	618.5	449.2	565.6	10.2
516.4	54.0	618.7	450.5	565.6	9.8
516.9	54.0	619.4	450.3	637.0	56.0
615.1	508.1	628.2	536.0	638.2	59.2
615.3	510.0	629.0	544.7	639.0	59.8
615.6	511.3			640.1	59.8
625.7	593.2	No. 4, $N_2 = 0.180$		640.5	61.2
626.1	595.2	549.8	53.4	712.5	273.9
627.2	595.6	550.6	54.4	712.6	276.1
628.2	602.6	553.5	58.2	712.8	276.9
629.0	609.9	555.7	60.8	713.2	278.6
		557.8	64.3		

The data are given in Table II. The first column gives the temperature in degrees Kelvin and the second the pressure in millimeters of mercury at 0° . The mole fractions of mercury and of potassium are represented by N_1 and N_2 , respectively.

These data, together with Smith and Menzies' data for pure mercury, are plotted in Fig. 2, and the equations for the straight lines which best fit the points for pure mercury and for each amalgam follow.

No.	N_1	Equation	
0	0	$\log p_1 = 7.841 - (3125/T)$	(1a)
1	0.0492	$\log p_1 = 7.799 - (3125/T)$	(1b)
2	0.0552	$\log p_1 = 7.779 - (3125/T)$	(1c)
3	0.0877	$\log p_1 = 7.717 - (3125/T)$	(1d)
4	0.180	$\log p_1 = 7.569 - (3212/T)$	(1e)
5	0.321	$\log p_1 = 7.968 - (3950/T)$	(1f)

These equations represent the individual pressures within 1-5%, usually 2-3%.

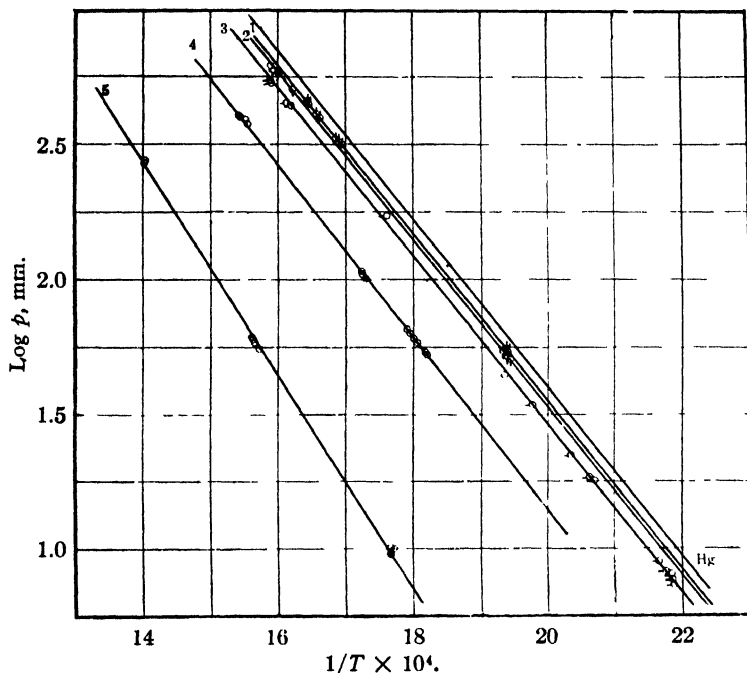


Fig. 2.—The vapor pressures of potassium amalgams.

In Table III are given the values of N_1 and of the activity, $a_1 = p_1/p_1^0$, of the mercury for each amalgam at 200, 250, 310 and 390°. The values of p_1 and p_1^0 were calculated from the equations for the vapor pressures of the amalgams and pure mercury.

TABLE III
THE ACTIVITY OF MERCURY IN POTASSIUM AMALGAMS

N_1	Temperature, °C.			
	200	250	310	390
0.951	0.908	0.908	0.908	0.908
.945	.867	.867	.867	.867
.912	.752	.752	.752	.752
.819	.349	.364	.378	.394
.679	.0241*	.0355*	.0515	.0762

* Supercooled solution.

The equation of van Laar, which is discussed by Hildebrand,⁷ was used to express the relation at each temperature between a_1/N_1 and the composition expressed as $r_1 = N_1/N_2$. The constants of the following equations were calculated from the data of Table III.

$$200^\circ \quad \log a_1/N_1 = -64.71/(1 + 2.689r_1)^2 \quad (2a)$$

$$250^\circ \quad \log a_1/N_1 = -28.94/(1 + 1.774r_1)^2 \quad (2b)$$

$$310^\circ \quad \log a_1/N_1 = -14.16/(1 + 1.209r_1)^2 \quad (2c)$$

$$390^\circ \quad \log a_1/N_1 = -7.041/(1 + 0.816r_1)^2 \quad (2d)$$

TABLE IV
COMPARISON OF PRESSURES CALCULATED FROM EQUATIONS 1 AND 2

Amal. no.	Eq. no.	Temperature, °C.			
		200	250	310	390
1	1b	15.56	66.70	275.0	1218
	2a-d	15.47	66.24	272.8	1206
2	1c	14.85	63.70	262.5	1164
	2a-d	15.16	64.92	267.3	1182
3	1d	12.88	53.95	227.6	1085
	2a-d	13.10	56.24	231.7	1025
4	1e	5.98	26.74	114.6	530.0
	2a-d	5.98	26.76	114.8	530.1
5	1g	0.41	2.61	15.57	102.4
	2a-d	0.41	2.60	15.60	102.6
Pure Hg	1a	17.15	73.52	303.0	1343
	Smith and Menzies	17.20	74.20	305.0	1336

Table IV gives the value of the vapor pressures calculated from the van Laar equation for each temperature and those calculated from the vapor pressure equations 1a-f. It will be noted that the agreement is about that of the agreement of equations 1a-f with the experimental data.

From the relation

$$\log \frac{a_2}{N_2} = \frac{\alpha_1 \beta_1}{(\beta_1 + r_2)^2} \quad (3)$$

where a_2 is the activity of potassium and $r_2 = N_2/N_1$, which Hildebrand⁷ has derived from the van Laar equation, the activities of the potassium can be calculated and an idea of the magnitude of the Henry's Law constant can be obtained by setting $r_2 = 0$, although the extrapolation is hardly to be recommended.

Fig. 3 is the plot of a_1 against N_1 for each of the four temperatures, the largest deviation from Raoult's law at each of the two highest concentrations being that corresponding to the lowest temperature.

Hildebrand has shown that $\log a_1/N_1$, for many systems, varies approximately linearly with N_2^2 . In Fig. 4 these quantities are plotted for each temperature and the best curves, which are more nearly straight lines for the highest temperatures than for the lowest, are drawn.

⁷ (a) van Laar, *Z. physik. Chem.*, **72**, 723 (1910); (b) **83**, 599 (1913). (c) Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1923, p. 45.

In order to calculate the e.m.f. of the potassium electrode we should have to calculate from Equation 3 the activity of potassium in a dilute

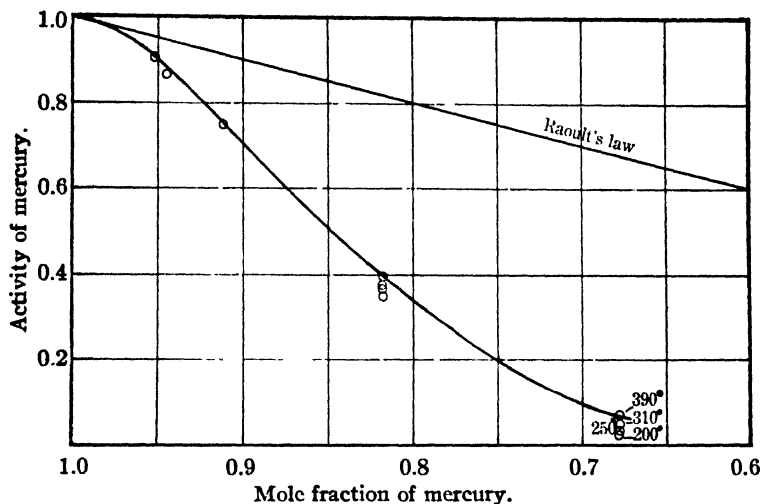


Fig. 3.—The activity of mercury in potassium amalgams.

amalgam at each temperature for which the constants are given in Equations 2a-d, find the activity of potassium in that amalgam at 25° by extra-

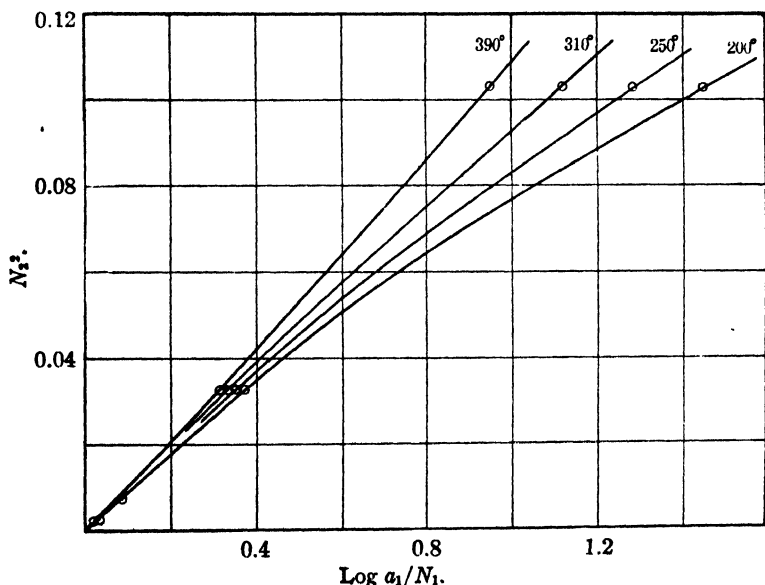


Fig. 4.—The variation of $\log a_1/N_1$ with N_1^2 .

polation and then measure the potential of the amalgam against some standard electrode. The last step has already been performed for a 0.2216%

potassium amalgam by Lewis and Keyes,⁸ but due to the fact that a_2 changes rapidly with the temperature, which a_1 does not, the extrapolation of the calculated values to 25° does not appear feasible.

It is of interest to note that, within the accuracy of these data, the heat of vaporization of mercury from the amalgams in which the concentration of potassium is as high as 8 mole per cent. is equal to that of pure mercury. This may be explained if we assume that a mercuride exists in solution, and that, with respect to pure mercury as the solvent, it is a perfect solute. Such may easily be the fact if a large number of atoms of mercury are chemically combined with or attached to each atom of potassium. This average number, calculated from the vapor pressure lowering and the concentration of the solution, is 9.44 for No. 1, 10.6 for No. 2 and 7.36 for No. 3. Evidently the analysis for No. 2 is low, a fact which accounts for the position for this amalgam on Fig. 3.

At higher concentrations than 8 mole per cent. the partial molal heat content of the mercury becomes negative, as is to be expected in solutions in which the deviations from Raoult's Law are so greatly negative, and the more so the higher the concentration of potassium.

Summary

The vapor pressures of mercury in equilibrium with five potassium amalgams have been measured. The concentrations ranged from 5 to 32 mole per cent. of potassium and the temperatures from 184 to 445°.

The equation of van Laar, which expresses the vapor pressure as a function of the concentration, temperature being constant, has been found to agree with the experimental data within the limits of accuracy of the latter.

The relative partial molal heat content of solvent mercury in the amalgams not exceeding 8 mole per cent. of potassium was found to be zero.

The deviations from Raoult's Law are among the greatest yet noted in any solutions and, as is to be expected, they decrease with rising temperature.

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⁸ Lewis and Keyes, *THIS JOURNAL*, **34**, 119 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR PRESSURE OF SODIUM AND CESIUM AMALGAMS

BY HENRY E. BENT AND JOEL H. HILDEBRAND

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The following investigation was undertaken as an extension of the work carried out by the senior author and his collaborators on the vapor pressures of amalgams in relation to the theory of metallic solutions.¹ It was hoped also that data might be secured which would permit the indirect determination of the e.m.f. of the cesium electrode.

The standard electrode potential of the alkali metals cannot be determined directly on account of the reaction between the metal and water. Lewis and Kraus² first showed that the electrode potential could be obtained by interposing a dilute amalgam of the alkali metal. The amalgam was used in aqueous solution with but little reaction with water. A second cell composed of an electrolyte other than water then gave the free energy change in going from the pure metal to the amalgam. The sum of the electromotive forces of the two cells gave the standard electrode potential.

This method was found successful with all the alkali metals except cesium. No solvent could be found for a salt of cesium which would not dissolve the metal. Consequently the method had to be abandoned. There seems to be no doubt that the e.m.f. of a dilute cesium amalgam could be measured against a hydrogen electrode using an aqueous electrolyte, so that the problem could be solved by an indirect determination of the e.m.f. between metallic cesium and the dilute amalgam. This could be accomplished by applying the Duhem equation to accurate data on the vapor pressure of cesium amalgams and so obtaining the relation between the activity of cesium and the composition of the amalgam. Some preliminary calculations showed that the results of the application of the Duhem equation would be sufficiently accurate to obtain satisfactory values for the activity of the cesium at the temperatures used in the investigation, although leaving somewhat doubtful the possibility of getting a sufficiently accurate temperature coefficient to make possible the extrapolation to 25°. An inspection of the freezing-point diagrams for the alkali metals led us to hope the hydrargyrites of cesium to be more dissociated than those of sodium, although the measurements showed this not to be the case.

The Materials Used

The sodium used was a good grade of commercial metal. No trace of other alkali metals was detected spectroscopically, nor could potassium be detected qualitatively, though one-tenth of one per cent. could have been observed.

¹ Hildebrand, "Solubility," A. C. S. Monograph, Chemical Catalog Co., New York, 1924, Chapter 16.

² Lewis and Kraus, *THIS JOURNAL*, 32, 1459 (1910).

The mercury was washed and distilled.

Kahlbaum's cesium bromide was tested spectroscopically for impurities without any positive test for metals other than cesium. The metal was prepared by mixing the dry salt with fresh calcium shavings in an iron tube. The tube was then placed in a glass tube, evacuated and heated to six or seven hundred degrees, which furnished a constant stream of cesium vapor. The metal was three times redistilled, leaving no residue the last time, and was found to melt above 25° in every case. The melting point of pure cesium is 26° .

The hydrogen was prepared by electrolysis of sodium hydroxide solution, dried by passing through concentrated sulfuric acid, phosphorus pentoxide and finally over an amalgam containing about eighty-five mole per cent. of sodium, which is liquid at room temperature. The hydrogen was then of sufficient purity to give no trace of oxide on the surface of the cesium in the upper part of the apparatus or in the tube containing the amalgam.

Experimental Method

The measurement of the vapor pressures was carried out essentially as in the previous work on vapor pressures of amalgams.³ The apparatus with which the cesium was to come in contact was thoroughly evacuated by a mercury vapor pump and well baked out. The cesium was contained in a small glass tube, as shown in Fig. 1, drawn out to a fine tip. After the glass had been out-gassed, the tip was broken by means of a weight controlled magnetically and the cesium allowed to run into the tube in which the pressure was to be measured. The mercury was then distilled into the cesium until the proper concentration had been attained.

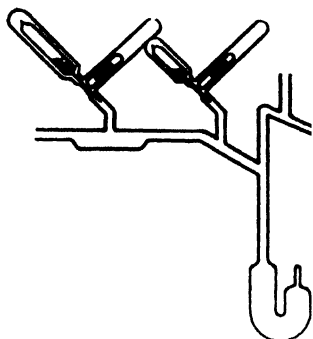


Fig. 1.—Apparatus for preparing amalgams and measuring vapor pressures.

The furnace was raised to the proper position, heated to the temperature of the run and the fused salt bath poured in. It was found convenient to filter the fused eutectic of sodium and potassium nitrate frequently through glass wool. After each run the salt was siphoned out of the furnace. The amalgam was allowed to heat for about an hour in order to eliminate part of the gas which might still be held by the glass. This was then boiled out and the amalgam allowed to stand for a time sufficient to allow the temperature to become constant and also to insure the amount of permanent gas above the amalgam being nearly constant during the run. Usually but four measurements of the pressure were taken on the amalgam and an equal number on the tube of pure mercury. This was sufficient to insure an accuracy due to chance errors of ob-

³ (a) Hildebrand, *Trans. Am. Electrochem. Soc.*, **22**, 319 (1913); (b) Hildebrand and Eastman, *This Journal*, **36**, 2020 (1914); (c) *ibid.*, **37**, 2452 (1915); (d) Hildebrand, Foster and Beebe, *ibid.*, **42**, 545 (1920).

servation and temperature fluctuations of the order of magnitude of 0.05%. Since other errors were larger than this it was not deemed advisable to take a greater number of measurements.

Inasmuch as a fluctuation of one degree in the temperature of the furnace changes the vapor pressure of the mercury by 3%, the furnace was designed with the intention of obtaining as constant a temperature as possible. Thus the bath which was the basis of the furnace was surrounded by three glass shields with horizontal layers of asbestos to prevent circulation of air. Two shields of asbestos paper outside the glass shields served to circulate the gases from the Fisher burner around the outside of the glass shields and to prevent radiation to the manometers. A gas pressure regulator maintained the gas pressure for the burner constant to within one-tenth of a millimeter. As a result the temperature remained constant during a run to within a few hundredths of a degree. The heating liquids were diphenylsulfone, anthraquinone, phenanthrene, diphenylamine and phthalic anhydride.

The analysis of the amalgam was carried out in such a way as to furnish with one sample two independent determinations of the mole fraction. The tube containing the amalgam was, therefore, first weighed and at the conclusion of the analysis the glass tube was weighed empty, thus giving the total weight of the amalgam. The amalgam was then treated with water until most of the alkali metal had been extracted and the solution poured into a flask to be titrated. The last of the alkali metal was removed by digestion with acid. Hydrochloric acid was found to dissolve some mercury in the presence of air. However, half normal sulfuric acid was found to have no appreciable effect even when mercury was boiled in it for more than an hour. The mercury distills with the steam in appreciable quantities during digestion, necessitating the use of a long-necked flask with a condenser, water cooled, inside the flask. A small tube prevented excessive bumping. A platinum wire was placed in contact with the amalgam near the end of the extraction to decrease the overvoltage of the hydrogen.

The acid was standardized against Kahlbaum's sodium carbonate, against sodium carbonate prepared by recrystallizing as bicarbonate and by weighing as sulfate. These methods agreed to within one tenth of one per cent. At the conclusion of the experiments the acid was again standardized.

The mercury was transferred from the long-necked digestion flask to a small casserole by pouring under water to prevent spattering. It was then washed three times with filtered acetone, dried by filter paper and transferred to a ten cubic centimeter weighing bottle by means of a watch glass pulled out to a spout which would enter the weighing bottle. This method of handling the mercury was found to be thoroughly dependable. The mercury was heated to constant weight by placing in an oven at 115° for five-minute periods, cooling in a desiccator and weighing. Longer periods for heating were found to result in distillation of the mercury.

The check on the analysis was obtained by subtracting the weight of either metal from the total weight of the amalgam to obtain the weight of the other metal. In the analysis of the sodium amalgams a further check was obtained by evaporation of the solution after titration and weighing the sodium sulfate.

Errors and Corrections

The causes of error have been carefully evaluated and corrections applied where possible. A consideration of these errors indicated that the

probable error of the measurements should be about 0.3%. This is about the average deviation observed in the experimental points from the smoothed curve. The methods of correcting for some of these errors will be discussed briefly.

One of the chief sources of error in vapor pressure measurements lies in the difficulty of obtaining a pure vapor. Rather than attempt to eliminate all vapors other than mercury a correction was applied. A small tip was placed on the end of the closed arm of the pressure tube which functioned in principle as the capillary of a McLeod gage. At the conclusion of each run the fixed gas was compressed into this tube and its pressure measured. The pressure of the fixed gas in the closed tube is given by the equation

$$p = H - (P + S + h\rho)$$

in which H is the pressure in the open arm as measured by the manometer, P is the pressure of the mercury in the amalgam, S is the capillary depression of the amalgam, h is the difference in height of the amalgam in the two arms of the tube and ρ is the density of the amalgam referred to mercury at 25° as unity. This pressure p usually varied from a few millimeters of mercury to two or three centimeters. The pressure of the fixed gas in the closed arm during the run was then found by multiplying this pressure by the ratio of the volume of the capillary tip to the volume of the vapor in the closed arm during the run. This ratio was of the order of magnitude of 1/30. Similar corrections were applied to the mercury tube and the final activity corrected by these two factors.

The chief source of error in making the above correction arises from assuming a density for the amalgam. It was necessary, therefore, to make measurements on the density, the data being recorded in Table I. The values are but approximate, as accurate values were unnecessary in this work and could not be obtained by the method used. It is interesting to note that the apparent molal volume of mercury in cesium appears to be negative until the concentration of mercury is more than thirty mole per cent.

TABLE I
DENSITY AND PARTIAL MOLAL VOLUMES OF CESIUM AMALGAMS

N_1 , mole fraction of mercury	ρ , density referred to mercury	N_1	\bar{V}_1 , partial molal volume of mercury, cc.	\bar{V}_2 , partial molal volume of cesium, cc.
0.937	0.85	1.0	14.8	42
.914	.80	0.8	13.3	57
.909	.84	.6	9.0	65
.877	.75	.4		69
.868	.77	.0		71
.779	.58			

Perhaps the greatest source of error was caused by the difficulty in sighting on the meniscus of concentrated amalgams. The amalgam

presented a flat or concave surface on amalgams in which the concentration of cesium was more than about ten mole per cent. As the concentration increased the wetting of the glass increased until in about thirty mole per cent. amalgams the glass would be completely covered by a film of the amalgam which, of course, made readings impossible. This film could be readily removed by heating with a burner, but that necessitated removing the amalgam from the bath and destroying the temperature equilibrium. In a few cases it was possible to improve the conditions by treating the glass before the run with hydrofluoric acid. The commercial 50% acid was found most satisfactory for this purpose, a short treatment at the boiling point sufficing to give good results in amalgams of moderate concentration. However, even in these it was necessary to sight on the contact of amalgam with glass rather than on the center of the meniscus. This might account for several tenths of a millimeter error in the case of the more concentrated amalgams.

The tube leading to the furnace was made small to cut down diffusion of mercury vapor and heated to prevent condensation. In this manner the error due to distillation of mercury was cut down to less than 0.1%.

At the higher temperatures the more concentrated sodium amalgams attacked the glass, making it necessary to take observations in as short a time as possible while the glass was transparent. No such difficulty was encountered with the cesium amalgams.

Experimental Results

The data for sodium amalgams were obtained before those for cesium amalgams and consequently the latter are a little more accurate. Furthermore, the bearing of the cesium measurements on the value of the cesium electrode potential made it desirable to obtain more measurements on cesium amalgams. So many improvements were made after the first ten runs that these were not considered of sufficient value to tabulate. All of the experimental measurements from run eleven on are given in the tables. Table II gives the experimental data obtained for sodium amalgams and also values calculated by methods to be described.

The first column gives the average temperature of the runs. The temperature varied during a run by perhaps a tenth of a degree or less. The temperature varied from one run to another by half a degree. The first variation is of greater importance, due to the fact that the vapor pressure of mercury varies by about 3% per degree change in temperature, while the activity of mercury in an amalgam changes at the rate of about 0.05% per degree.

The second column of the table gives the mole fraction of mercury as obtained by the analysis. The two methods of obtaining the number of moles of mercury usually varied by about one part in ten thousand.

The two values obtained for the number of moles of sodium usually varied by about one part in a thousand. The third column gives the experimental values of p/p° .

TABLE II
ACTIVITY OF MERCURY IN SODIUM AMALGAMS

T	N_1	p/p° , obs.	1 p/p° , -----	2
648.1	0.872	0.701	0.686	0.701
	.627	.080	.080	.080
	.611	.066	.067	.065
608.5	.961	.941	.938	.942
	.939	.894	.888	.894
	.872	.692	.678	.688
	.773	.348	.351	.355
	.740	.272	.263	.264
	.541	.016	.021	.018
	.529	.021	.017	.015
	.511	.011	.013	.011
	.774	.343		.340

TABLE III
ACTIVITY OF MERCURY IN CESIUM AMALGAMS

T	N_1	p/p° , obs.	1 p/p° , calcd.	2
651.4	0.940	0.865	0.856	0.833
	.909	.733	.733	.738
	.711	.090	.085	.083
609.9	.926	.800	.792	.800
	.877	.558	.571	.568
	.847	.417	.435	.423
	.831	.358	.370	.355
	.751	.129	.129	.134
	.713	.072	.070	.073
573.9	.914	.733	.731	.731
	.865	.495	.495	.493
	.728	.079	.076	.078
553.6	.937	.838	.824	.837
	.934	.822	.804	.820
	.868	.487	.488	.481
	.779	.153	.155	.149

The data from cesium amalgams given in Table III seem to be a little more accurate than those for sodium amalgams in the lower range of concentration, but inferior in the range of higher concentration. This was doubtless due to the greater tendency of the cesium amalgams to wet the glass. The temperature control was somewhat better than in the work on sodium. The variation of the temperature during a run was usually not more than one or two hundredths of a degree, while the variation of

the temperature from one run to another was less than three tenths of a degree. The values of N_2 are probably in error by 0.1% or less.

Interpretation of Results

The experimental data may be treated in a variety of ways. The most obvious way to show deviations from Raoult's law is to plot activity against mole fraction. This has been done in Fig. 2, in which the activity of mercury is plotted against its mole fraction. As is evident from the figure, this method of plotting does not permit extrapolation far beyond the region of experimental measurements.



A more useful method of plotting such data is to consider the deviations from perfect solution. For this purpose $\log a_1/N_1$ may be plotted against some function of N_1 . If Raoult's law is obeyed, the plot is a straight line, $\log a_1/N_1$ being zero. It is very convenient in many instances to plot $\log a_1/N_1$ against N_2^2 .⁴ Some of the data are so represented in Fig. 3, the points falling almost exactly on a straight line. The straight line is dotted in the figure, while the full curve is the best smooth curve which could be drawn through the experimental points.

The last columns of Tables II and III have been calculated from these curves. The fourth column of Table

II has been calculated by means of the equation $\log a_1/N_1 = \frac{1}{2}\beta N_2^2$. The value of the single constant $-\beta$,

obtained graphically, is 12.81 at 648.1°K. and 13.33 at 608.5°K. The values in the fourth column of Table III were obtained in the same manner, assigning values to $-\beta$ of 22.16, 24.74, 26.52 and 28.66 for the four temperatures, the smallest value being for the highest temperature.

The values in the last column of Table II were obtained by a more roundabout method, but one which furnishes information concerning the relative partial molal heat contents of the amalgams and also fits the

⁴ (a) Ref. 1, p. 48; (b) Hildebrand, *Proc. Nat. Acad. Sci.*, 13, 267 (1927).

experimental data better. The method consisted in first obtaining an equation which better fitted the experimental data for the temperature common to the greatest number of runs. Second, from this equation and the experimental values at other temperatures, the variation of the activity with the temperature was obtained. Third, from the change of activity with the temperature the relative partial molal heat content of mercury in the amalgams was obtained, which was then plotted against

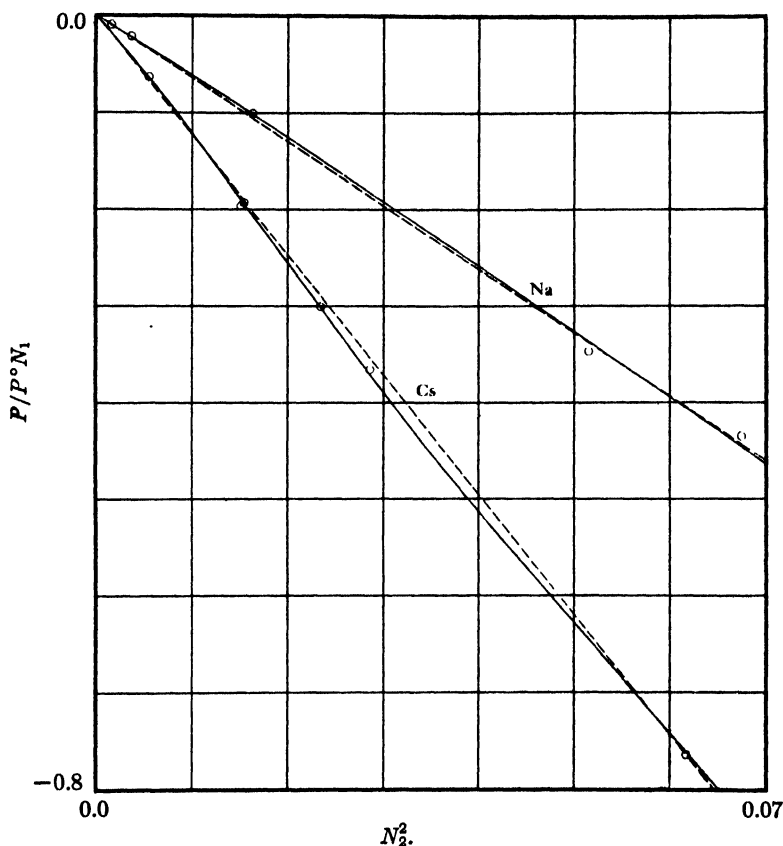


Fig. 3.—The activity of mercury in sodium and cesium amalgams.

mole fraction and a smooth curve used to recalculate the activity at any temperature and concentration.

The empirical equation which best fitted the experimental data is $\log a_1/N_1 = 2.082 (\log N_2 + 0.418)$. The value of the coefficient of $\log N_2$ gives an idea of the difference to be expected between the values given in the last two columns of Table II. A similar plot for the cesium data indicated a similar value for the coefficient of $\log N_2$ in dilute amalgams, but one which approached 2 in the more concentrated amalgams. The

values at 608.5°K. in the sixth column of Table II were obtained from this equation.

From the above equation values of the activity were calculated at concentrations used in runs at other temperatures. The change in $\log a_1$ with respect to $1/T$ multiplied by 2.303/1.988 gives the relative partial molal heat content of mercury in the amalgam, referred to pure mercury as the standard state. These values vary with the concentration and may be represented by the equation $\bar{L}_1 = 4300 N_2^2$. Table IV gives the values obtained by the above method and those calculated from the equation, while Table V gives similar values for cesium. These values are subject to a rather large percentage error, inasmuch as the change of activity with the temperature is slight.

TABLE IV

RELATIVE PARTIAL MOLAL HEAT
CONTENT OF MERCURY IN SODIUM
AMALGAMS

N_1	\bar{L}_1	
	Obs.	Calcd.
0.128	-76	-81
.226	-204	-255
.373	-665	-694
.389	-765	-752

TABLE V

RELATIVE PARTIAL MOLAL HEAT
CONTENT OF MERCURY IN CESIUM
AMALGAMS

T	N_1	\bar{L}_1	
		Obs.	Calcd.
592	0.086	-107	-56
	.135	-122	-136
	.272	-572	-548
582	.063	-32	-49
	.067	-28	-54
	.132	-211	-210
	.221	-560	-588

The values in the last column of Table II were calculated by this method and agree considerably better with the experimental points than those calculated by means of the more simple equation. The activity of mercury may now be calculated in an amalgam of any concentration and at any temperature, the accuracy depending on the range of extrapolation. If the range of extrapolation is great, doubtless the simpler equation would alone be justified.

In considering the data on cesium amalgams no simple empirical equation was found to represent the data accurately throughout the whole range studied. The curve was, therefore, treated in two portions, in the range from $N_1 = 1$ to $N_1 = 0.8$ being represented by the equation $\log a_1/N_1 = 8.954 N_2^2 + 42.40 N_2^3 - 110.3 N_2^4$ and in the range of more concentrated amalgams by the equation $\log a_1/N_1 = 7.793/(1 + 0.7267 r_1)$ in which r_1 is defined as N_1/N_2 . The curves representing these two equations differ but slightly, but since the change of activity with the temperature is but slight it is essential to fit the experimental points as well as possible. The accuracy obtained in determining the relative partial molal heat content is greater for sodium amalgams than for cesium amalgams. The

latter were found to be represented by the equation $\bar{L}_1 = AN_2^2$, in which the value for A was taken as 10,000, 6400 and 10,400 for the temperature intervals between the various runs, the first value being for the highest temperature. The values in the last column of Table V were calculated by means of these equations. Similar calculations were carried out by merely sliding a cut-out curve and gave values differing little from those calculated as above.

The Activity of the Alkali Metal

The calculation of the activity of the solute from the known activity of the solvent may be accomplished by either the graphical or analytical integration of the Duhem equation.⁵ The former is accomplished by plotting $\ln a_1/N_1$ against N_1/N_2 . The equation used is

$$\ln a_2/N_2 = - \int \frac{N_1}{N_2} d \ln a_1/N_1$$

The latter method consists in expressing $\ln a_1/N_1$ as a function of N_2 and integrating analytically. In these calculations a_2 , the activity of the alkali metal, will refer to the pure liquid metal as the standard state. On substituting the value of $\ln a_1/N_1$, namely $2.303\beta N_2^2/2$, and integrating we obtain the relation

$$\ln a_2/N_2 = 2.303[-\beta(N_2 - \frac{1}{2}N_2^2) + \frac{1}{2}\beta]$$

The right-hand member of this equation is identical with minus $\frac{1}{2}\beta N_1^2$.^{4a} The form of the equation first given has been used in the calculations since the term involving N_2^2 can be neglected for small values of N_2 . For a given value of N_2 the e.m.f. of a cell in which the reaction is the transfer of sodium to amalgam of this concentration is then given by the relation

$$E = \frac{RT \ln a_2}{23074}$$

If we take N_2 as 0.01772, we find the e.m.f. of such a cell to be 1.07 volts at 648.1° and 1.03 volts at 608.5°K. If we extrapolate such a value over the long range to 298° we obtain the value 0.72 volt. Such a cell has been measured by Lewis and Kraus and was found to have the e.m.f. of 0.85 volt. The assumption used in the above extrapolation is that dE/dT is constant over the range of extrapolation, which undoubtedly is incorrect. Lewis and Kraus determined dE/dT at 298°. If an average value of dE/dT is taken for the extrapolation, the e.m.f. is found to be 0.88 volt.

The foregoing calculations are of value in determining the reliability of similar calculations of the cesium cell. More data are available for the cesium calculations, but the difficulties of extrapolation are greater than for sodium due to the lower activity of the mercury in these amalgams.

⁵ (a) Hildebrand and Eastman, *THIS JOURNAL*, **37**, 2452 (1915); (b) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Compounds," McGraw-Hill Book Co., New York, 1923.

Using the various empirical equations which expressed the experimental data, we find for the e.m.f. of the cell in which the reaction is a transfer of pure cesium into an amalgam whose concentration is 1.0 atom per cent. 1.43 to 1.47 volts at 609°K. Upon extrapolating to 25° we find a value of 1.71 volts, the agreement of the various methods of extrapolating being to the order of 0.05 volt. A further idea of the accuracy of such calculations may be obtained from Fig. 7.

The Deviation of Sodium, Potassium and Cesium Amalgams from Raoult's Law

It has been shown in Fig. 3 that the vapor pressure of mercury from sodium and cesium amalgams may be represented by the equation

$$\log a_1/N_1 = \frac{1}{2}\beta N_2^2 \quad (1)$$

in which β is a constant which varies with the temperature. The activity of the solute may be calculated from Equation (1) and the Duhem equation, giving

$$\log a_2/N_2 = -\beta(N_2 - \frac{1}{2}N_2^2) + \frac{1}{2}\beta \quad (2)$$

Equation (1) was derived from data extending over a concentration range of $N_1 = 1$ to $N_1 = 0.5$. We may test Equation (2) by means of the data obtained by Richards and Conant on sodium amalgams at 25°.⁶ They measured the e.m.f. of cells in which the reaction is a transfer of sodium from one amalgam to another of different concentration. These data give activities of sodium in amalgams referred to each other or, by extrapolation, referred to infinite dilution. For the test of Equation (2) it is necessary to have the activity referred to pure sodium as the standard state. This may be accomplished by combining the data of Richards and Conant with those of Lewis and Kraus.² The latter have measured the e.m.f. of a cell in which the reaction is the transfer of sodium into a dilute amalgam. Since $E/0.05915 - \log N_2$ differs from $\log a_2/N_2$ by a constant factor, the two sets of data may be combined by plotting $E/0.05915 - \log N_2$ as ordinate against N_2 as abscissa and shifting the curve along the ordinate until it coincides with the single measurement of Lewis and Kraus of $\log a_2/N_2$. The resulting curve is A in Fig. 4. The experimental points fall on a straight line almost within the limits of experimental accuracy. This has been observed for similar data on barium amalgams by Anderson.⁷

That these points should fall on a straight line for small values of N_2 is evident from Equation (2), for when N_2 is small the term N_2^2 may be neglected. The slope of the curve gives the value for the constant β and the departure of the intercept at $N_2 = 0$ from $\frac{1}{2}\beta$ indicates the departure to be expected from Equation (1) for large values of N_2 . The equation for the curve through the experimental points in Fig. 4 is log

⁶ Richards and Conant, *THIS JOURNAL*, 44, 601 (1922).

⁷ Anderson, *ibid.*, 48, 2285 (1926).

$a_2/N_2 = 20N_2 - 12.8935$. This value of β is in good accord with the values found at higher temperatures.

These data serve to emphasize again the importance of the constant β which expresses the deviation of both solvent and solute from Raoult's law.^{4b} The more exactly Equation (1) corresponds to vapor pressures throughout the whole range of concentration the more nearly will the intercept in Fig. 4 equal one-half the slope of the curve. The value of the intercept gives the log of the ratio of the activity of sodium in infinitely dilute amalgam to pure sodium.

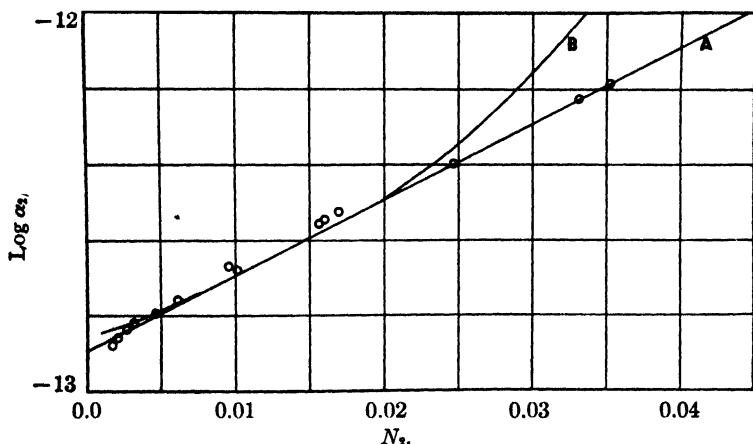


Fig. 4.—Activity of sodium in sodium amalgam at 25°.

The value of β obtained from Fig. 4 makes possible the calculation of the vapor pressure of mercury from liquid sodium amalgams at 25°, using the equation $\log a_1/N_1 = -10N_2^2$. Poindexter⁸ has measured the vapor pressure of solid sodium amalgams, using the ionization gage. His data may be represented by an equation of the form of that above in which the constant at 298°K. is -22 ± 5 . As would be expected, the escaping tendency from a solid amalgam is much less than from a supercooled liquid amalgam. Poindexter found much higher vapor pressures in the case of the dilute liquid amalgams.

Table VI gives values of β for sodium and cesium amalgams obtained from the experimental work of this paper. The value for sodium at 298° is obtained from the data of Richards and Conant. The value for cesium at 298° is obtained by extrapolation. The values for potassium are obtained from the data of Millar.⁹ The value for barium is obtained from the data of Anderson.⁷ Barium and cesium amalgams seem to vary from perfect solution to about the same extent. There is quite a difference,

^{4b} Poindexter, *Phys. Rev.*, **28**, 208 (1926).

⁹ Millar, *THIS JOURNAL*, **49**, 3003 (1927).

TABLE VI

THE DEVIATION OF AMALGAMS FROM RAOULT'S LAW AS EXPRESSED BY β IN THE EQUATION $\log a_1/N_1 = \beta N_2^2$

Amalgam	Temp., °K.	$-\beta$
Sodium	648.1	12.82
	608.5	13.33
	298.1	20.0 ± 0.4
Potassium	663.1	19.0
	583.1	20.4
	523.1	21.8
	473.1	23.6
Cesium	651.4	22.16
	609.9	24.74
	573.9	26.52
	553.6	28.66
Barium	298.1	55.0 ± 1.0
	298.1	55.0

however, between cesium and sodium amalgams. The data of Table VI have been plotted in Fig. 5. It thus appears that the value for β is about the same for a sodium amalgam at 298°K., a potassium amalgam

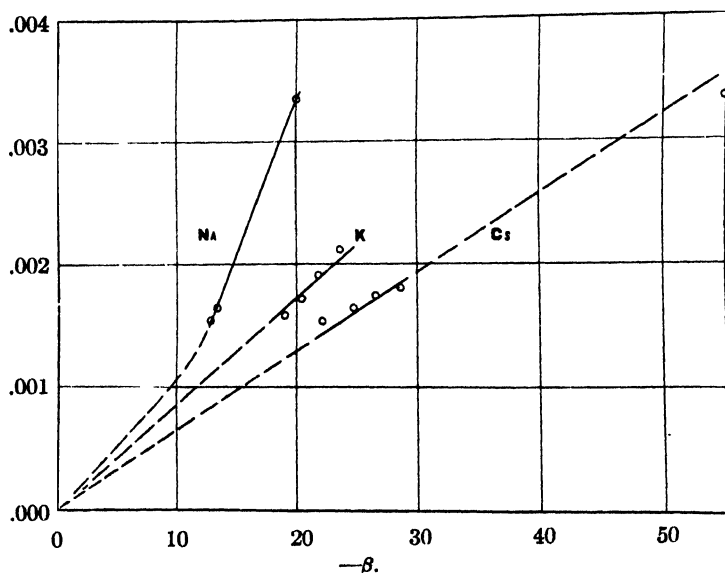


Fig. 5.—The variation of $-\beta$ (in the equation $\log a_1/N_1 = \beta N_2^2$) with the temperature.

at 580° and a cesium amalgam at 770°. Doubtless the curves in Fig. 5 should not be straight lines, but since the data are not of sufficient accuracy to determine the curvature it has seemed better to draw them so. A straight line implies that the relative partial molal heat content of the

mercury is independent of the temperature. The equations for these curves are: $\beta_{\text{Cs}} = 15,620/T$, $\beta_{\text{K}} = 11,630/T$ and $\beta_{\text{Na}} = 3930/T + 6.84$. Combining these equations with Equations (1) and (2) (simplified) we obtain the expressions

$$\begin{aligned}\log a_1/N_{1\text{Cs}} &= -\frac{7810}{T} N_2^2 \\ \log a_1/N_{1\text{K}} &= -\frac{5815}{T} N_2^2 \\ \log a_1/N_{1\text{Na}} &= -(1965/T + 3.42) N_2^2 \\ \log a_2/N_{2\text{Cs}} &= -\frac{15,620}{T} N_2 + C \\ \log a_2/N_{2\text{K}} &= -\frac{11,630}{T} N_2 + C \\ \log a_2/N_{2\text{Na}} &= -(3930/T + 6.84) N_2 + C\end{aligned}$$

The expressions for the activity of the mercury a_1 are supported by experimental data up to a concentration of $N_2 = 0.5$. The expressions for the activity of the solute are of use in this simplified form to a concentration of $N_2 = 0.05$. Using the more exact expression of Equation (2), or its equivalent $\log a_2/N_2 = -1/2\beta N_1^2 + C'$, values for the activity of the solute may be obtained up to a concentration of $N_2 = 0.5$. The value of the constant C has been obtained only in the case of sodium amalgams at 25° , in which case it has been found to be 12.8935.

Compound Formation

Departure from perfect solution has frequently been explained by the assumption of compound formation.¹⁰ A large number of compounds have been shown to exist¹¹ in the solid phase for sodium amalgams, suggesting the calculation of the vapor pressure of amalgams from these data.

Fig. 6 gives three curves, A, B, C, calculated by assuming in each case the formation of one compound, namely, NaHg_2 , NaHg_4 and NaHg_{16} . The first two of these compounds are indicated by the cooling curve while the compound NaHg_{16} merely indicates an approximate formula which would be necessary to explain the behavior of dilute amalgams if only compound formation is considered. It will be observed that through a limited range each curve corresponds more or less closely with the smooth curve through the experimental points. In more dilute solutions the first two curves give too high an activity, and in more concentrated solution too low an activity. The second of these deviations may be accounted for to some extent by assuming dissociation of the compound. This has been done in Curve D, Fig. 6, by assuming the equilibrium constant $K = a_{\text{NaHg}_2}/a_{\text{Na}}a_{\text{Hg}}^2 = 1000$. By assuming similar dissociation for the other

¹⁰ Ref. 1, p. 72.

¹¹ Schüller, *Z. anorg. Chem.*, **40**, 385 (1904).

compounds it is possible to approach the experimental data through a narrow range of concentration, the agreement suggesting that compound formation is involved, but the results are far from satisfactory.

Doubtless the true state of affairs is to be represented by the existence of a large number of compounds simultaneously, each with its characteristic dissociation constant. The attempt has been made to see to what extent such an assumption accounts for the behavior of the amalgams.

The following solution of the problem has been suggested by Professor Scatchard and is based on the assumption of definite compounds, dissociating in accord with the mass law, each molecular species obeying Raoult's law.

"Given a system made up from 1 mole of sodium and n moles of mercury. The activity of the mercury is a ; the number of moles of mercury in the system is (Hg); the number of moles of sodium (0); the number of moles of NaHg_2 (2); of NaHg_4 (4); of NaHg_6 (6). We have the following equations

$$(2) = Ka^2(0) \quad (1)$$

$$(4) = K'a^4(0) \quad (2)$$

$$(6) = K''a^6(0) \quad (3)$$

$$n = (\text{Hg}) + 2(2) + 4(4) + 6(6) \quad (4)$$

$$1 = (0) + (2) + (4) + (6) \quad (5)$$

From (5)

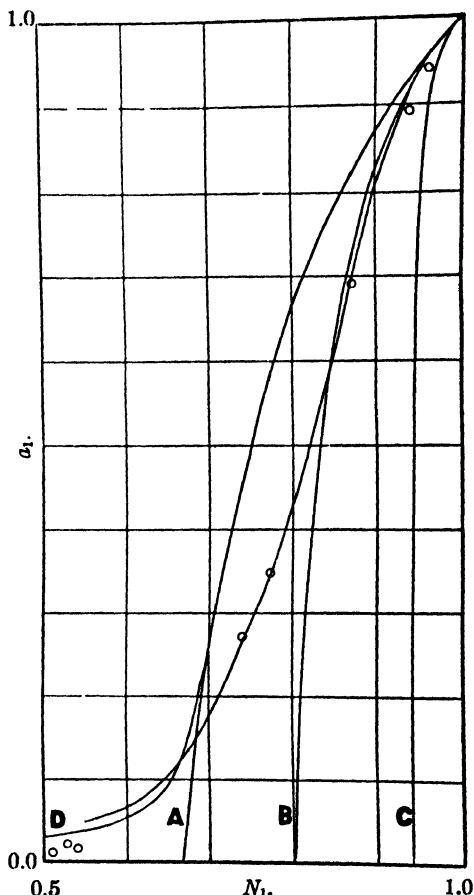
$$\frac{\text{Hg}}{1 + (\text{Hg})} = \frac{a}{1 - a} \quad (6)$$

Substituting from Equations (1), (2) and (3) in (5) gives

$$1 = (1 + Ka^2 + K'a^4 + K''a^6) \cdot (0) \quad (7)$$

Substituting from (1), (2), (3), (6) and (7) in (4) gives

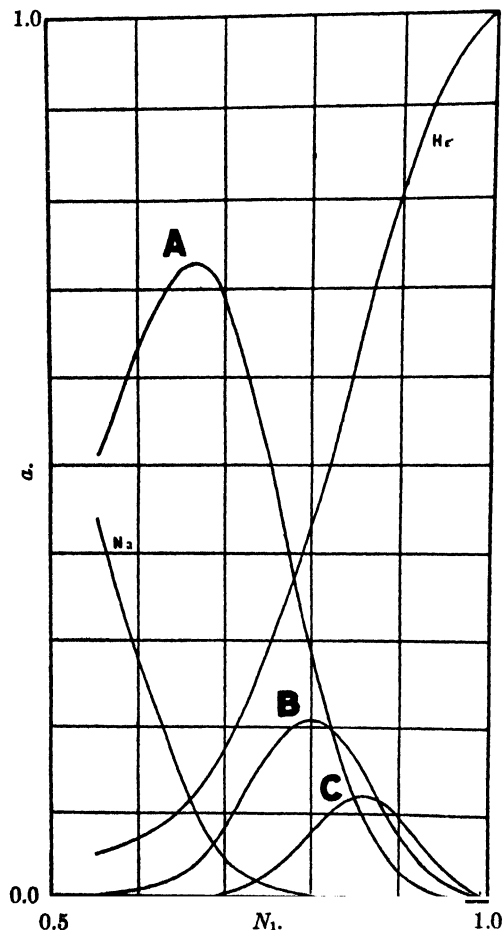
$$n = \frac{a}{1 - a} + \frac{2Ka^2 + 4K'a^4 + 6K''a^6}{1 + Ka^2 + K'a^4 + K''a^6} \quad (8)$$



Curves A, B and C are calculated by assuming complete formation of the compounds NaHg_2 , NaHg_4 and NaHg_6 , respectively, while D is calculated by assuming partial dissociation of NaHg_2 .

Fig. 6.—The activity of mercury calculated by assuming compound formation, compared with experimental values.

By means of Equation (8) very good agreement with the experimental data was obtained for a limited range of concentration by allowing K'' to equal zero and determining K and K' by successive approximations. The smooth curve through the experimental points in Fig. 6 is calculated



Curves A, B and C represent the mole fraction of NaHg_2 , NaHg_4 and NaHg_{16} , respectively.

Fig. 7.—The constituents of sodium amalgam calculated by assuming three compounds existing simultaneously.

suggests that n may be larger than 15.7. Millar has pointed out that n may be larger than 10 for potassium amalgams. It is interesting to note that if no change in atomic volume is experienced on the formation of such a compound, there is room on the surface of a sodium atom for 16 mercury atoms. A further test of the validity of the assumption of this compound is obtained

by assigning values to all three constants and agrees, within the limits of experimental error, with the experimental data from $a_1 = 0.1$ to $a_1 = 0.9$. The values chosen for the constants are as follows: $K = 500$; $K' = 2000$; and $K'' = 4000$.

The assumptions involved in the above calculations are that there are five molecular species present in a sodium amalgam and that these all obey Raoult's law. Doubtless other compounds are present and other factors would have to be considered for an exact treatment of the behavior of these amalgams. It is interesting, however, that such a simple picture should account so well for their behavior. A clearer idea of the constitution of the amalgams suggested by these calculations is obtained from Fig. 7. In Fig. 7 the activity (or mole fraction) of each constituent is plotted against the mole fraction of mercury in the amalgam.

The existence of such a compound as NaHg_{16} (C, Fig. 6) is also suggested by the work of Poindexter. This author suggests

by calculating the dissociation constant for the compound from the measurement of Lewis and Kraus and then calculating the data of Richards and Conant from this constant. Curve B, Fig. 4, has been calculated in this manner and agrees within the limits of experimental error to a concentration of $N_2 = 0.02$. The value found for the dissociation constant is 12.8579.

Summary

1. The vapor pressures of sodium and cesium amalgams have been measured at temperatures from 554 to 651°K. and at concentrations from $N_1 = 1$ to $N_1 = 0.5$. The data may be represented by the equation $\log a_1/N_1 = KN_2^2/T$.

2. The relative partial molal heat content of mercury in the amalgams has been calculated from the temperature coefficient of the activity, making possible the calculation of the free energy of transfer of mercury in amalgams at intermediate temperatures and over the range of concentration studied.

3. Approximate values have been obtained for the free energy of transfer of alkali metal to amalgam.

4. Values of the constant β , which expresses the deviation of both solvent and solute from Raoult's law, are compared for sodium, potassium, cesium and barium.

5. The whole of the deviation from perfect solution exhibited by sodium amalgams can be explained on the assumption of compound formation. The compounds NaHg_2 , NaHg_4 and NaHg_6 explain the vapor pressure of amalgams from an activity of 0.1 to 0.9, while in very dilute amalgams the compound NaHg_{16} explains both vapor pressure and e.m.f. data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXV. ARC SPECTROGRAPHIC DETECTION AND ESTIMATION OF GERMANIUM. OCCURRENCE OF GERMANIUM IN CERTAIN TIN MINERALS. ENARGITE AS A POSSIBLE SOURCE OF GERMANIUM¹

BY JACOB PAPISH, F. M. BREWER AND DONALD A. HOLT

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Arc Spectrographic Detection and Estimation of Germanium

The emission spectrum of germanium contains a number of persistent lines which, as is the case with all metals and with a few non-metals, lie in the optical spectral range. These lines serve admirably for the detection of small quantities of germanium, and in connection with some of the less persistent lines they can be used in the quantitative estimation of this element. A direct current arc of about half a kilowatt made between two electrodes of pure graphite was used for spectral excitation. The spectrograms were prepared with the aid of a quartz spectrograph of the Littrow auto-collimating type² using double-coated ortho photographic plates.³ 1.4408 g. of pure germanium dioxide was introduced into water, solution being effected with the aid of the least amount of potassium hydroxide, and the volume was made up to 100 cc., thus furnishing a solution containing an equivalent of one gram of germanium per 100 cc. From this stock solution, solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 g. of germanium per 100 cc. were prepared. The arc discharge was passed between the graphite electrodes for a few moments; it was then interrupted, to allow the electrodes to cool somewhat, and while the latter were still warm, a small, definite portion of each solution was placed on the lower electrode. These portions consisted of one-tenth cc. of solution and were delivered from a calibrated capillary pipet holding in all 0.12 cc. and divided into fiftieths of a cubic centimeter. Different electrodes and a separate plate were used for each concentration, one spectrogram of the blank arc and four of the arc charged with the germanium material being obtained on a single plate. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

This article is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as Article No. 6 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

² Made by Adam Hilger, Limited, London.

³ Made by Eastman Kodak Company, Rochester, N. Y.

0.0001 mg. of germanium, respectively. The spectral lines observed at the different concentrations are given in Table I. In this table, as well as in those that follow, v signifies that the line in question is visible and f that it is faintly visible. The decrease of intensity has been brought about by the decrease of the quantity of material in the zone of excitation. The investigation was limited to the spectral range between λ 4682 and λ 2198 Å.

TABLE I
SPECTRAL LINES AT DIFFERENT CONCENTRATIONS

λ	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg.	λ	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.
4685.9	f					2644.2	v	v		
4226.6 ^a	v	v	v	v		2592.5	v	v	v	v
3269.5	v	v	v	f		2589.2	v	f		
3124.8	v	v				2556.3	v			
3067.0	v	v				2533.2	v	v		
3039.1	v	v	v	v	v	2498.0	v	v		
2829.0	v	f	f			2436.4	v			
2793.9	v					2417.4	v	v	v	f
2754.6	v	v	v	v		2397.9	f			
2740.4	v	v				2394.1	f	f		
2709.6	v	v	v	v		2359.2 ^c	v	v	f	
2691.3	v	v				2338.6	f	f		
2651.6	v	v	v	v	f	2327.9	f			
2651.1 ^b	v	v	v	v	v	2314.2	v	f		
						2198.7	v	f		

^a Because of the low dispersion of a prism spectrograph in this range, λ 4226.6 of germanium is indistinguishable from λ 4226.7, a persistent line of calcium.

^b C. W. Gartlein of the Department of Physics, Cornell University, found that the wave length of this line is 2651.2 Å.

^c The wave length of this line was determined by C. W. Gartlein.

If germanium in any form in quantities larger than one milligram, be subjected to arc excitation, λ 2389.5, λ 2379.1, λ 2256.0 and λ 2246.4 will be visible in addition to the lines included in Table I. As seen from this table λ 3269.5, λ 2754.6, λ 2709.6 and λ 2417.4 are visible when 0.001 mg. of germanium is introduced into the arc, while λ 3039.1, λ 2651.6 and λ 2651.1 persist when one-tenth of this quantity is used. The *raies ultimes* of de Gramont⁴ are among these lines.

Occurrence of Germanium in Certain Tin Materials

Germanium-tin mixtures were prepared by mixing water solutions of germanium dioxide and stannous chloride in such proportions as to have 0.0001 mg. of germanium with tin varying in quantity from 0.01 mg. up to one milligram. Similar mixtures with higher germanium concentrations, using fixed alkali germanates, were also prepared. As ex-

⁴ De Gramont, *Compt. rend.*, 171, 1106 (1920). See also Foote and Mohler's "The Origin of Spectra," The Chemical Catalog Company, Inc., New York, 1922, p. 143.

pected, the presence of tin had no influence upon the spectral lines of germanium except in cases of lowest germanium concentration. When 0.0001 mg. of this element in a mixture with tin was subjected to spectral excitation, the persistent lines of germanium were much fainter than when germanium alone is used. Twelve tin minerals⁵ were subjected to arc spectrographic examination for the presence of germanium in the following manner. They were ground finely and definite quantities of each were introduced into the arc. These quantities varied from 6 to 10 mg. Several successive exposures were obtained from each mineral sample without replenishing the arc with fresh material; in this way it was observed that in the case of some of the minerals lines due to germanium were present in the first spectrogram only, while in the case of others they also appeared in those that followed. The results which were obtained from an examination of the spectral range between λ 3040 and λ 2590 are summarized in Table II.

TABLE II
GERMANIUM LINES IN SPECTROGRAMS OF TIN MINERALS
Range examined, λ 3040– λ 2590

Mineral and source	3039 1	2651 6	2651 1	2592 5	Ge, estd.
Cassiterite, San Joge Mine, Loyaza, La Paz, Bolivia		f	f		0.001
Stream tin, Buck Creek, Alaska					Absent
Cassiterite, north of Battle Mountain, Nevada					More than 0.005
Cassiterite, Clive County, Mole River, New England, N. S. W.		f	f		0.001
Cassiterite, Ena Mino, Japan					Negligible
Cassiterite, Burra Tumbarumba, N. S. W.					Absent
Cassiterite, Hot Springs, Lower Tanana River, Alaska	f				Negligible
Cassiterite, Cornwall, England	f				Negligible
Stream tin, Durango, Mexico	v	v		f	0.005
Wood tin, Dawson, Yukon Territory	v	f			0.001
Cassiterite, Bakerville, Queensland	Absent
Cassiterite, King Mountain, North Carolina	Absent

Eight of the twelve tin minerals subjected to spectrographic analysis were found to contain traces of germanium. The estimated percentage of germanium in these minerals, which is given in the last column of Table II, was obtained as follows. A record was made of the spectral lines of germanium as observed in connection with each mineral. It was then assumed that a definite weight of germanium, say in milligrams, capable of yielding these particular spectral lines was present in the zone of excita-

⁵ Kindly supplied by Dr. David White of the U. S. Geological Survey.

tion. Knowing the quantity of each mineral subjected to excitation it was a simple matter to estimate its germanium content. This method has been found in our Laboratory to give fairly satisfactory results in a good many cases where the element to be estimated quantitatively is present in traces. It is important that minimum quantities of the crude material or mixture containing the element in question be introduced into the arc.

TABLE III
GERMANIUM LINES IN SPECTROGRAMS OF ENARGITE
(Range examined, λ 3040- λ 2498)

Enargite No.	3039.1	2754.6	2740.4	2709.6	2691.3	2651.6	2651.1	2644.2	2592.5	2589.2	2533.2	2498.0	% Ge, estd.
1	v	v		v	f	v	v	f	v			v	More than 0.01
2	f					f	f						Less than 0.001
3													None
4	v	f		f		v	v		f				More than 0.001
5	v	v		v		v	v		v			f	0.01
6	v	v		v		v	v		v			f	0.01
7	v	v		v	f	v	v	f	v			f	More than 0.01
8	f												Negligible
9	v	v		v		v	v		v				0.01
10	v					f	f						Less than 0.001
11	v	v	v	v	v	v	v	f	v	f	f	v	More than 0.1
12	v	v		v	f	v	v	f	v			f	0.01
13	v	f		f		"	"		f				More than 0.001
14	v	v	v	v	v	v	v	f	v	f	f	f	0.1
15	v					f	f						Less than 0.001
16													None
17													None

- No. 1. Enargite from Central City, Colorado.
 No. 2. Enargite from Butte, Montana.
 No. 3. Enargite from Ouray County, Colorado.
 No. 4. Enargite from Butte, Montana.
 No. 5. Enargite from Butte, Montana.
 No. 6. Quartz and pyrite gangue from No. 5.
 No. 7. Enargite from Braden Copper Company, Chile.
 No. 8. Pyrite gangue from No. 7.
 No. 9. Enargite from Red Mountain, Ouray County, Colorado.
 No. 10. Gangue material from No. 9.
 No. 11. Enargite from Santa Fé Mine, Chiapas, Mexico.
 No. 12. Enargite from Shoebridge Lode, Tintic District, Utah.
 No. 13. Enargite from Rising Star, Nevada.
 No. 14. Enargite from Butte, Montana.
 No. 15. Enargite from Shoebridge Lode, Tintic District, Utah.
 No. 16. Pyrite gangue from No. 15.
 No. 17. Enargite from Montana.

" Because of the extremely high lead content of this ore, the lead line λ 2651.7 was so wide that it completely obstructed the two germanium lines $\lambda\lambda$ 2651.5 and 2651.1.

Enargite as a Possible Source of Germanium

Enargite is a fairly common copper-bearing mineral in which this element is combined with arsenic and sulfur and associated with traces of other elements. Specimens of this mineral from various localities were investigated spectrographically for the presence of germanium. The method followed was similar to the one used in connection with the tin minerals and the results are recorded in Table III.

Since some of these ore minerals were available in comparatively large quantities, work was undertaken to extract germanium from them. The ore was ground finely, placed in a Pyrex distilling flask and decomposed with nitric acid. The contents were heated to dryness over a steam-bath, sulfuric acid was added and heat was applied until the oxides of nitrogen were driven off. Hydrochloric acid was then added and the whole saturated with chlorine and distilled in a slow current of this gas. Samples of the residue were tested from time to time spectrographically for the presence of germanium and the distillation was discontinued when germanium was found to be totally absent or present in negligibly small traces. The distillate which contained germanium tetrachloride was collected in a cooled receiver and saturated with hydrogen sulfide. The germanium disulfide thus obtained was removed and converted to the dioxide.

The method developed by Dennis and Johnson⁶ was used to determine germanium quantitatively in some of the enargite ores. It was necessary, however, to modify this method slightly in its initial stage. The weighed sample of enargite was decomposed in the manner just described in connection with the extraction of germanium from this mineral. The residue, freed from the oxides of nitrogen, was subjected to the hydrochloric acid-chlorine distillation. Determinations made on two samples of enargite gave the following results:

	Enargite No. 1	Enargite No. 5
Weight of enargite	50 g.	100 g.
Weight of GeO_2 extracted	0.0238 g.	0.0192 g.
Percentage of germanium	0.033	0.013

The enargite minerals dealt with in the present investigation contained much less germanium than the rare minerals argyrodite, canfieldite and germanite. Nevertheless, enargite, because of its availability, can be used as a source of this element. In school laboratories where students do experimental work with the so-called rarer elements, enargite can be made to serve as the crude material from which to extract germanium. In view of the variation of the germanium content in the different samples of enargite, it is possible that some enargites not as yet investigated are considerably richer in germanium. Ordinary copper of commerce is

⁶ Dennis and Johnson, *THIS JOURNAL*, 47, 790 (1925).

known not to contain germanium, and since large quantities of copper are obtained from enargite, it is not impossible that at some stage of smelting or refining the germanium contained in the ore is concentrated in some waste product or by-product. We know that this happens in the case of certain zinc ores containing minute traces of germanium; these traces are increased to a very appreciable content in a by-product during the process of smelting.⁷ It is our intention to extend the present investigation to copper smelter materials in hope of finding germanium in a form more concentrated than in the original enargite.

Summary

The arc spectral lines of germanium and the concentrations at which they appear were given.

The presence of traces of germanium in certain tin ores was noticed. A method was given for the estimation of traces of germanium.

Germanium was found to be present in appreciable traces in certain varieties of enargite.

A method for the extraction of germanium from enargite was described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE INFLUENCE OF RADIATION ON THERMAL UNIMOLECULAR REACTIONS

By JOSEPH E. MAYER

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Introduction¹

The concept of molecules of high energy content as the reacting molecules in chemical reactions was first introduced by Arrhenius² primarily to explain the high temperature coefficient of most reactions. Although this theory has been generally accepted, there has been considerable dispute as to whether the mechanism of activation is by collisions between molecules or by the absorption of radiation. The radiation hypothesis, first suggested in a rather vague form by Trautz³ and later elaborated by W. C. McC. Lewis⁴ and by Perrin⁵ appeared to be much strengthened by

⁷ See Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); Dennis and Papish, *Z. anorg. Chem.*, **120**, 1 (1921).

¹ A brief statement of the results of this investigation (excepting the last and most convincing experiment) has been published in a paper by G. N. Lewis and J. E. Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623 (1927).

² Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

³ Trautz, *Z. wiss. Phot.*, **4**, 160 (1906).

⁴ W. C. McC. Lewis, *J. Chem. Soc.*, **109**, 796 (1916); **111**, 457 (1917); **113**, 471 (1918).

⁵ Perrin, *Ann. phys.*, [9] **11**, 1 (1919).

investigations of Hirst and Rideal⁶ who showed that the specific rate of the unimolecular decomposition of nitrogen pentoxide was as high or higher at very low pressures than at normal concentrations.

Various investigators⁷ have pointed out that the observed reaction rate demands a higher rate of activation than seems likely to be afforded by radiation even under favorable circumstances. Lewis and Smith⁸ showed that in the case of nitrogen pentoxide a high coefficient of absorption for radiation over a considerable range of the spectrum would account for the observed rate if the absorption of radiant energy alone were responsible for activation.

Later, measurements of absorption coefficients for nitrogen pentoxide in the infra red to wave lengths of about 7μ were published by Daniels.⁹ These were much lower than the values found necessary by Lewis and Smith⁸ to account for the observed decomposition rate. However, the absorption showed a noticeable trend, increasing with the wave length in the range studied. In view of this, and the fact that the greater part of the energy in the spectrum at room temperature lies at longer wave lengths, it was considered advisable to make rough measurements on the absorption coefficients farther in the infra red. The experiments are described and the results given later in this paper.

Daniels¹⁰ also measured the decomposition rate of nitrogen pentoxide exposed to the radiation from a Nernst glower, and found no increase in rate other than that due to the rise in temperature of the gas. This would be expected on the modified form of the radiation hypothesis in which it is postulated that the energy of activation is acquired, not by the absorption of one high energy quantum by a molecule of average energy, but by the consecutive absorption of many quanta of low energy. At normal pressures, collisions of the second kind would distribute the energy of partially activated molecules between successive quantum absorptions according to the Maxwell distribution law, raising the temperature of the gas. The rate would then at all times be determined by the measured temperature of the mass of the gas. Experiments of this type are also open to the objection that the effective radiation may be wholly absorbed by a very thin layer of the gas at the high pressure employed and not reach the main body of the reacting material.

Professor G. N. Lewis suggested that it would be advisable, therefore, to study the influence of radiation on the rate of a unimolecular reaction in the absence of collisions, and at such low concentrations that the absorption would not materially affect the density of radiation of any fre-

⁶ Hirst and Rideal, *Proc. Roy. Soc. (London)*, **109A**, 526 (1925).

⁷ See, for example, Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

⁸ Lewis and Smith, *THIS JOURNAL*, **47**, 1508 (1925).

⁹ Daniels, *ibid.*, **47**, 2856 (1925).

¹⁰ Daniels, *ibid.*, **48**, 607 (1926).

quency throughout the reacting material. In order to do this a molecular stream was employed. Because of the necessity of maintaining the rectilinear nature of the stream it was considered inadvisable to employ nitrogen pentoxide or any molecule which breaks into two or more parts at the moment of reacting.

Pinene was therefore used, the racemization of which had been shown by Smith¹¹ to be one of the most satisfactory unimolecular reactions.

A similar experiment on the dissociation of iodine molecules in a molecular stream under the influence of radiation was performed by Kröger.¹² In this case, however, the order of the reaction at normal pressures has not been determined. Later work¹³ on the heat of activation of the reaction from considerations of band spectra data makes possible recalculation of Kröger's data. This has been done and the results are recorded later in this paper.

The Total Absorption Coefficient of Nitrogen Pentoxide for Infra Red Radiation

Apparatus.—The study of absorption spectra at long wave lengths is made difficult by the fact that all materials which may be used as windows and prisms at shorter wave lengths absorb too highly for applicability in the extreme infra red. A very simple apparatus without windows was suggested by Professor Lewis with which determinations could be made of the coefficient of total absorption over all the black body spectrum at low temperatures. The source consisted of a black body kept at constant temperature, and the receiver was a sensitive thermopile.

Owing to the absence of windows a vacuum thermopile could not be used. The thermopile employed consisted of eight "Ideal" to "Manganin" junctions. The thermopile was some three inches long and could be slipped down the neck of an ordinary 500cc. flask as shown in Fig. 1; it was rigidly attached to a glass stopper, a glass tube carrying the leads out of the apparatus. The flask in which the thermopile was enclosed was blackened on the inside with lampblack and was placed in a metal container so that it could be completely surrounded with ice and water. A short neck through which the thermopile could be illuminated, projected from the side of the flask through the walls of the container. A sensitive galvanometer was connected to the thermopile, the deflection of which was read directly and used as a measure of the radiation intensity.

The absorption cell consisted of another 500cc. flask with two short necks sealed at opposite sides and projecting through the ends of a trough which surrounded the cell. The ends of the two necks which were flush

¹¹ Smith, *THIS JOURNAL*, **49**, 43 (1927).

¹² Kröger, *Z. physik. Chem.*, **117**, 387 (1925).

¹³ Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

with the ends of the trough, were closed by sliding shutters. The shutter at the end facing the thermopile could be filled with ice and water in order to maintain it at the same temperature as the rest of the wall surrounding the junctions.

The radiator was a glass flask, coated outside with lampblack, in which water or any other liquid could be boiled to maintain it at constant temperature.

Experiments.—By observing the galvanometer deflection at definite times after opening the shutter, the absorption coefficient was determined with pure dry air and with nitrogen pentoxide at known pressure in the absorption cell. After twenty seconds the galvanometer had prac-

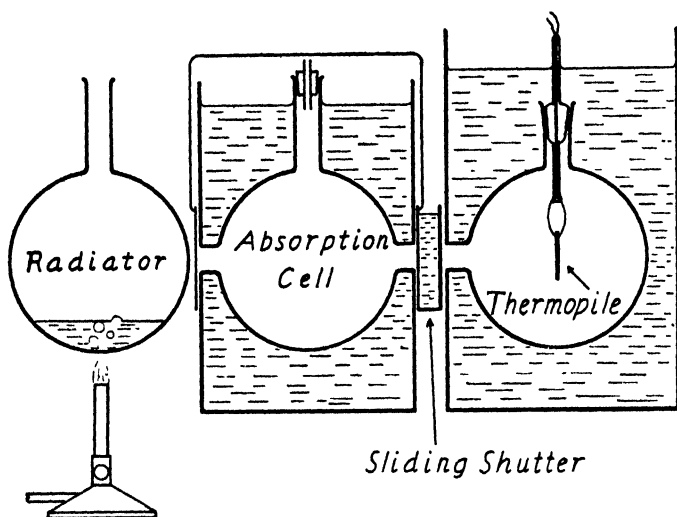


Fig. 1.

tically come to equilibrium; the ratios of the two deflections, both at twenty seconds or both at thirty seconds, gave the same results within the limit of experimental error.

The partial pressure of nitrogen pentoxide was maintained by placing crystals of it with phosphorus pentoxide in the bottom of the cell, and in addition slowly introducing dry air which had been passed over crystals at the same temperature as the cell. The large volume of the cell compared with the small openings at the ends, some two square centimeters' cross section, together with the slow addition of gas, was considered sufficient to maintain a constant pressure over the short period of time the shutters were opened.

Boiling water and boiling acetophenone (202°) were used as temperature controls for the radiator.

Table I shows the recorded data for a typical experiment.

TABLE I
 DATA OF A TYPICAL EXPERIMENT

Time	Galvanometer scale readings in tenths of mm. for time in sec. from opening of shutters						Galvanometer deflections from zero time in tenths of mm.		Average deflections and fraction transmission	
	0	10	15	20	25	30	0-20	0-30		
Air	10	170	195	203	204	207	193	197		
	10	180	200	205	209	210	195	200	194.5	199.5
	10	175	200	206	210	211	196	201		
									0.746	0.757
N ₂ O ₅	10	130	150	155	160	160	145	150	145	151
	10	140	152	155	160	162	145	152		
									0.756	0.757
Air	10	170	190	201	205	210	191	200	192	199.5
	12	168	189	203	209	211	193	199		
									0.735	0.742
N ₂ O ₅	12	135	148	153	158	160	141	148		
	18	130	148	158	160	163	140	145		
	19	140	155	162	167	169	143	150	141	148
	19	130	151	160	165	168	141	149		-
									0.735	0.733
Air	02	170	189	193	200	203	191	201		
	07	170	192	199	208	210	192	203	192	202
	10	178	196	205	209	212	195	202		
	12	178		203	208	214	191	202		

The absorption cell was 14.3 cm. long and the pressure of nitrogen pentoxide (26.8°) was 495 mm., the black body at 202°.

The ratios for the thirty-second and for the twenty-second deflections represent the fraction transmission of the gas. These agree with each other within the limits of experimental error, the values at thirty seconds being generally the more reliable. The average of these is taken as the result for this experiment.

 TABLE II
 SUMMARY OF EXPERIMENTAL RESULTS

Exp. no.	Temp. of cell °C.	Press. of N ₂ O ₅	Transmission, <i>F</i>	Temp. of radiator, °C.	Coeff. of abs. $\alpha = \frac{\log 1/F}{c \times l}$
					cm. ² molecules ⁻¹
1	24.6	410	0.769	100	1.25×10^{-21}
2	0.0	51	.825	100	7.32
3	26.8	495	.747	100	1.16
4	0.0	51	.808	100	8.27
5	.0	51	.849	100	6.36
6	.0	51	.872	202	5.37
7	20.0	275	.689	202	2.65
8	27.0	500	.713	202	1.32
9	27.0	500	.743	202	1.18
10	0.0	51	.805	202	8.26
11	.0	51	.818	202	7.64
12	.0	51	.716	202	12.61
13	.0	51	.786	202	9.20

Owing to the fact that the transmission was measured directly, the absorption, which is the logarithm of the reciprocal of the transmission, could not be obtained with any accuracy at low pressures. Even at 0° , at which temperature the pressure is 51 mm. and the absorption about 9.2%, the results were extremely erratic. Table II shows a summary of the experimental results.

In Table II, Col. 1 is the number of the experiment, Col. 2 the temperature of the absorption cell, which temperature controls the pressure of nitrogen pentoxide given in Col. 3. Col. 4 is the transmission, or fraction of the total energy incident on the thermopile after passing through the cell containing nitrogen pentoxide. Col. 5 is the temperature of the black body radiator. The value of the absorption coefficient ($\log 1/F)/c \times l$, in which c is the concentration in molecules per cc. and l is the length of the cell (14.3) in cm., is given in Col. 6.

Results.—The value of α obtained in Table II is found to be the same within the experimental error for the black body radiator at 100 and 202° . It is also found to be of the same order of magnitude as the absorption observed by Daniels⁹ for wave lengths shorter than 7μ .

The coefficient of absorption is the α of the equation

$$\frac{E_1}{E_2} = e^{\alpha \times l \times c} \quad (1)$$

in which E_1 is the energy incident upon, and E_2 the energy transmitted by, a cell of length l containing gas at a concentration c . This equation is strictly true only for energy of single frequencies. The α of Table II is the average of the α 's for all frequencies obtained, not by integrating the differential equation

$$\frac{\partial E_\nu}{E_\nu} = \alpha_\nu \times c \times dl \quad (2)$$

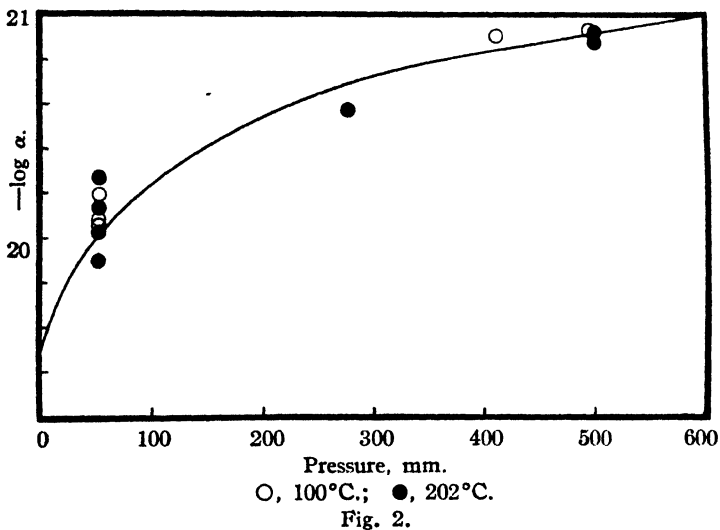
for all frequencies, but by determining the average α found in the integrated form. The α_0 or average of the α_ν in the differentiated form, which would experimentally be the α at zero values of concentration times length of cell, would be expected to be larger than the values found at high pressures. To estimate the value of α_0 , the logarithm of α has been plotted against the pressure in Fig. 2 and the curve obtained has been extrapolated to the axis of zero pressure. The antilogarithm of the intersection has been taken as the most probable value of $\alpha_0 = 3 \times 10^{-20}$.

Although the value of α_0 so obtained may be in error ten-fold, the observations are sufficiently accurate for the purpose of the experiment. In the units in which α_0 is expressed it represents the fraction of a beam of black body radiation one square centimeter in cross section which would be extinguished by a single molecule of nitrogen pentoxide. The maximum value of α_0 calculated by Lewis and Smith⁸ is the cross section of the quantum as derived from their equation

$$\alpha_0 = \sigma = \frac{\lambda^2}{8\pi} = \frac{c^2}{8\pi \nu^2} \quad (3)$$

Taking the wave length $\lambda = 9\mu$ as that corresponding to the greatest energy in the black body spectrum at 300°K. , we find that by equation (3) the cross section $\sigma = 3.2 \times 10^{-8} \text{ cm.}^2$ is found to be 10^{12} times the value of α_0 found in this experiment.

Using the maximum value of the absorption coefficient from their equation, Lewis and Smith⁸ calculated the reaction rate constant of nitrogen pentoxide to be $3 \times 10^2 \text{ sec.}^{-1}$ at 300°K. , which is 10^7 -fold greater than the experimental value of $4 \times 10^{-5} \text{ sec.}^{-1}$. The absorption coefficient determined experimentally should then be expected to give a rate of



about 10^5 -fold too little. Calculations have been made, assuming nitrogen pentoxide to be a molecule of 14 degrees of freedom, as do Lewis and Smith, integrating the number of molecules absorbing quanta of sufficient energy to activate them over the total number of molecules, and using the same absorption coefficient for all molecules and all wave lengths. The value of the rate constant $K = 1 \times 10^{-10} \text{ sec.}^{-1}$ so obtained is smaller than the experimental by a factor of 2.5×10^{-6} .

The Racemization of Pinene under the Influence of Radiation

Apparatus.—For the determination of the racemization of pinene under the influence of radiation in a molecular stream, a micro-polarimeter tube, the capacity of which was only one-tenth of a cubic centimeter, was used in the measurement of the optical rotation. It was necessary to collect about three-tenths of a cubic centimeter on the receiving surface to allow for the loss in transferring the liquid and in filling the tube. Stern¹⁴ showed that in a molecular stream determined by two slit orifices the

¹⁴ Stern, *Z. Physik*, 39, 751 (1926).

maximum concentration in the stream was independent of the width of the first orifice, hereafter called the nozzle to avoid confusion with the second, or defining, orifice. This is necessitated by the fact that the maximum pressure which may be permitted in the gas behind the nozzle is such that the mean free path of the molecules is of the order of magnitude of the width of the slit, in order to avoid collisions after emission into the first chamber. In the case of a nozzle of circular cross section, however, the maximum obtainable concentration in the stream will increase with the diameter of the nozzle, since the quantity of gas flowing through at any given pressure increases with the cross-sectional area, or square of the diameter of the nozzle; whereas the maximum permissible pressure decreases with the first power of the diameter. The stream will then be expected to remain perfectly defined by the geometrical design of the apparatus, and the

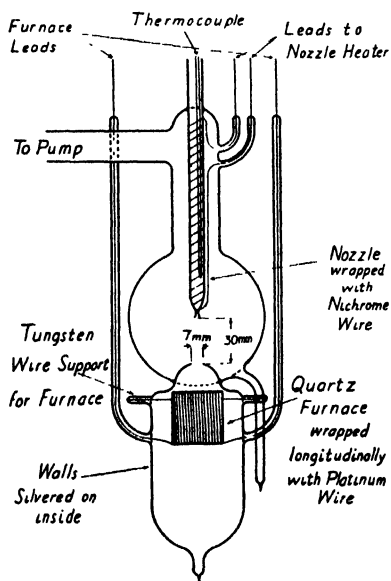


Fig. 3.

quantity of material incident on the receiving plate will increase directly with the pressure up to this threshold value. Above this pressure the stream loses its perfect definition and becomes fuzzy at the edges. It was found experimentally, however, that the amount of material collected on the receiver increased directly with the pressure far above this maximum pressure. At these higher pressures the radius from the nozzle, beyond which the concentration of the gas is so low that no collisions between molecules take place, can be calculated, and this radius, rather than the diameter of the nozzle, is the significant factor in determining the dimensions of the stream. Since perfect definition of the stream was not required in this experiment, but merely the inclusion of all but a small fraction of the pinene within certain limits, to avoid contact with the furnace, the experiments were performed with a greater pressure behind the nozzle than would be permissible for most molecular stream work.

The molecular stream apparatus was constructed of Pyrex glass, as shown in Fig. 3. A tube wrapped with nichrome wire and having a thermocouple inside of it projected downward into a chamber; the end of the tube, drawn to a nozzle, was 3 cm. above the center of a circular orifice 7 mm. in diameter which defined the stream. Below this orifice the stream passed into a glass tube about 6 cm. in diameter which carried the furnace and on the bottom of which the pinene impinged. The bottom of this tube was drawn to a fine teat for convenience in draining. The complete apparatus was immersed in liquid air during the experiments. The nozzle had a smallest diameter of one millimeter and flared outward slightly after the design of steam turbine nozzles. The first chamber was connected by means of short glass tubing over 2 cm. in diameter through a liquid-air trap to a mercury-vapor vacuum pump which pumped directly into a high vacuum line evacuated by a second such pump. A McLeod gage measured the pressure in this secondary vacuum line, the construction of the lines being such that the pressure in the apparatus was less than one quarter that measured in the gage.

To produce the radiation field a cylindrical quartz tube 33 mm. in diameter and 35 mm. high was nicked at the ends with a saw and wound longitudinally inside and out with platinum wire. About 390 cm. of wire 0.508 mm. in diameter, making 55 complete turns, was used. The furnace was supported in the chamber by its heavy copper leads

and by five tungsten wires, projecting radially inwards from short side tubes in the wall of the chamber. The inner walls of the chamber were silvered to reduce loss of radiation to the liquid air. A voltmeter connected to the leads into the furnace, together with an ammeter in series with the circuit, permitted measurements of the energy input.

Experiments.—The pinene used was distilled several times into liquid air under a high vacuum to remove residual gases. Immediately before the experiment sufficient material for the run was redistilled into a container connected to the nozzle. The apparatus was well baked out, surrounded with liquid air and the nozzle and furnace heated to the desired temperature. The pinene was then allowed to pass through the nozzle at 4mm. pressure by lowering a mercury trap.

During the course of the experiment frequent observations were made of the temperature of the nozzle, which was maintained within 3 of 93°, and of the amperes flowing through the furnace and the voltage at the leads. In the last experiment made at the highest temperature the ammeter reading was 6.1 amperes with a maximum variation of 0.1 ampere, and the voltmeter read 53.2 volts with a variation of 1 volt. The pressure was measured, by means of the McLeod gage, frequently during the experiment and was always observed to be less than 10^{-4} mm. after the experiment had been going on for a few minutes. As before mentioned, the pressure in the apparatus was probably less than one quarter of this value.

When all the pinene had passed into the apparatus the furnace current was stopped and air permitted to enter the chambers. The liquid air was removed and the pinene drawn out of the bottom of the furnace chamber by breaking the teat.

During all distillations of pinene, mercury from the traps collected on the liquid-air cooled surface with the pinene and formed a black, colloidal solution. After standing for an hour, the mercury settled to the bottom, leaving clear pinene. The liquid collected in the apparatus was similarly black at first but after standing became as clear as the original sample.

If pinene were allowed to strike the furnace at the temperature of the experiment sufficient decomposition resulted to create a marked increase in pressure. The fact that the pressure remained low during the course of the experiments was considered sufficient proof that no appreciable quantity of pinene touched the furnace. There was always observed a slight increase in pressure at the beginning of the experiment, probably due to traces of residual gases in the liquid.

About 4 cc. of pinene passed through the nozzle per hour, three hours being necessary to collect sufficient material at the receiving surface to insure ease of analysis.

After the experiments were completed a black thermocouple was sealed into the bottom of the furnace chamber. The temperature observed in the center of the furnace under conditions duplicating an experiment recorded the density of radiation through which the stream passed. During the course of the experiments, due largely to the distillation of platinum from the furnace and to several minor accidents of operation, the silvered walls of the furnace chamber had become blackened. Calculations at that time showed them to be less than 50% reflecting. Undoubtedly during the experiments, especially the earlier ones performed when the mirrored walls were in good condition, the density of radiation was much higher than that about to be calculated, making the results even more conclusively unfavorable to the radiation hypothesis than the succeeding calculations would indicate. The resistance of a piece of the same platinum wire that was used in the furnace was determined at 0°, at 100°, and at 444.6°. This calibration and the measured resistances of the furnace at 0° and during the experiments made possible fairly accurate estimates of the average temperature of the platinum wire when the furnace was in operation.

About six experiments in all were completed, the radiation density in the furnace chamber corresponding to temperatures of from 830°K. to 1053°K. In none of the

experiments was there a detectable racemization. The optical rotation could be measured in the micro-polarimeter tube which was used to an accuracy of about 3%.

Conclusions

The geometrical dimensions of the furnace were such that it subtended the 0.726 part of the complete solid angle about a point in the center. The platinum wire covered 0.270 of the total area of the inside surface of the quartz. From this, and from an equation given by Geiss¹⁵ for the emissivity of platinum at the temperature T ,

$$E = \gamma T^{\phi} \sigma T^4 \quad (4)$$

in which $\gamma = 6.22 \times 10^{-4}$, $\phi = 0.767$, and σ is the Stefan Boltzman radiation constant, it was calculated that the energy density of radiation emitted from the platinum wire should be, at a point in the center of the furnace,

$$U_{Pt} = 0.726 \times 0.270 \times \gamma \times T_{Pt}^{\phi} \times C \times T_{Pt}^4 \quad (5)$$

in which CT^4 is the density of radiation in a hohlraum completely surrounded by walls at the temperature T .

Assuming quartz to be 90% a black body, since the temperature was such that most of the emitted radiation was of longer wave length than the limit of transparency, the contribution of the quartz to the radiant energy at a point in the center was calculated to be

$$U_Q = 0.726 \times 0.730 \times 0.900 \times C \times T_Q^4 \quad (6)$$

The actual density of energy was known to be

$$U_T = C \times T_{th}^4 \quad (7)$$

from the measured temperature T_{th} of the thermocouple. Using the average temperature of the platinum wire determined from the resistance data for T_{Pt} , and equating the sum of equations (5) and (6) to equation (7), the temperature of the quartz, T_Q , was evaluated.

The density of energy of various frequencies in a hohlraum at the temperatures T_{Pt} and T_Q was calculated from the Planck equation, the densities for T_{Pt} were multiplied by the factor $(0.726 \times 0.270 \times \gamma \times T_{Pt}^{\phi})$, and those for T_Q by $(0.726 \times 0.730 \times 0.900)$; the two were then added. The results for the different experiments were represented by curves of densities plotted against frequencies.

To determine the lowest temperature at which pinene should show noticeable racemization in the time of the experiment, use was made of the experimental equation relating the specific reaction rate constant K to the absolute temperature T .

$$K = ke^{-h\nu/KT} \quad (8)$$

in which $\nu = 4.60 \times 10^{14} \text{ sec.}^{-1}$, the frequency corresponding to the energy of activation, 43,710 calories, found by Smith,⁸ and k is a constant having the value $2.6 \times 10^{14} \text{ sec.}^{-1}$.

¹⁵ Geiss, *Physica*, 5, 203 (1925).

From the velocity of the molecules leaving the nozzle and the length of the radiation field, the time during which the molecules were exposed to the radiant energy was calculated to be 1.2×10^{-4} sec. Using this time and assuming that the reaction could be detected if it progressed 6% (about twice the experimental error in reading the polariscope), the value which the reaction rate constant K would have in order that the pinene should be racemized was calculated to be 431 sec.^{-1} . This value was used in equation (8) and T_m , the minimum temperature at which pinene should show appreciable (6%) racemization in the time for which it was exposed to the radiation of the furnace, was determined to be 800°K .

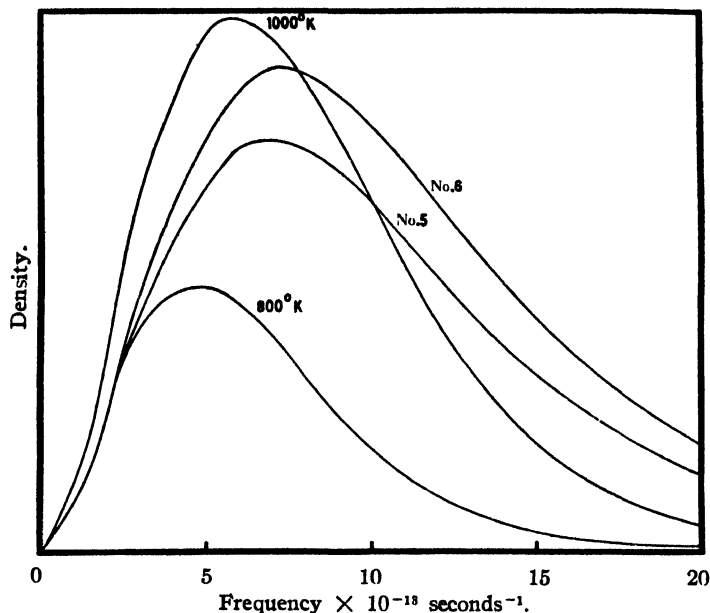


Fig. 4.

In Fig. 4 the curve for the energy density of radiation plotted against the frequency as calculated from the Planck equation is given for $T = 800^\circ$. Curves 5 and 6 in the same figure are the curves for the distribution of radiation in the furnace chamber under the conditions of Experiments 5 and 6, the highest temperatures at which observations were made. In these experiments the average temperatures of the platinum wire were 1700°K . and 1790°K ., respectively, the temperature of a black body in equilibrium with the radiation in the center of the chamber 1004°K . and 1053°K ., and the calculated temperature of the quartz 1065°K . and 1123°K ., respectively.

The curves show that for Experiment 5 above frequencies of 3×10^{18} [$\lambda = 10\mu$] and for Experiment 6 above frequencies of 2×10^{18} [$\lambda = 13\mu$]

the radiation in the furnace chamber is of greater density than in a hohlraum at 800°K. The curve for radiation in a hohlraum at 1000°K. is also shown in the figure. At this temperature only the 10^{-6} part of the pinene should have remained unracemized. The greater part of the curves of both experiments lies above the curve for 1000°K.

Kröger¹² has attempted to measure the dissociation of iodine in an apparatus similar to the one employed in this research, using a cylindrical platinum furnace. Calculations were made on the basis of these data, using a theoretical heat of activation not available to Kröger at the time of publication. Franck¹³ has shown that the energy to which an iodine molecule must be raised by the absorption of radiation in order to dissociate is greater than the heat of dissociation by 22,000 cal. Using the heat of activation thus calculated, 57,000 cal., we may estimate the rate of dissociation of iodine at any temperature by the use of the equation first proposed by Dushman¹⁴

$$K = \nu e^{-h\nu/KT} \quad (9)$$

which differs from Equation (8) only in the substitution of ν for the experimentally determined k . This equation has been found to agree closely with the experimental rate constants of all the unimolecular reactions so far investigated, and although all theoretical derivations so far advanced may be objectionable it appears to be empirically applicable to unimolecular rate constants.

Kröger states that in his experiments no dissociation was observed and that the accuracy of his measurements was of the order of 1%. Following the method employed with pinene and assuming the length of his radiation field to be 6 cm., and the velocity of the molecules to correspond to 29.3°, we find the T_m in this case to be 934°K. Kröger estimates the temperature of his furnace in the experiment at the highest temperature to be 1300°K. At this temperature the density of radiation of frequency 6×10^{14} , chosen as a convenient reference since it is the frequency corresponding to the heat of activation, is about 10^4 -fold the density of the same frequency at 934°K. The density in the furnace chamber of all frequencies must be smaller than that calculated for 1300°K. by some factor dependent on the shape of the furnace employed, and for sufficiently low frequencies this factor would decrease the density to a lower value than that corresponding to a hohlraum at 934°K. It, nevertheless, appears evident that the rate of dissociation of iodine by radiation alone is much slower than that calculated by Equation (9).

In the case of iodine the rate of dissociation, by radiation, using the calculated heat of activation, is lower than the rate of reaction normally found in thermal reactions of the same energy of activation, whereas the

¹⁴ Dushman, *THIS JOURNAL*, 43, 397 (1921).

experiment with pinene shows that using the known (extrapolated) rate, radiation alone does not cause reaction.

Theoretical Discussion

The results of these experiments appear definitely to show that in neither of the two reactions considered, the decomposition of nitrogen pentoxide or the racemization of pinene, can the activation by the absorption of radiant energy alone be of sufficient rapidity to play an important role in the reaction.

It should be pointed out, however, that in the calculations of the probable rate of activation by collisions as made by Rice and Ramsperger¹⁷ the chance that one molecule of energy ϵ will acquire an additional energy $\Delta\epsilon$ in one collision drops rapidly as the value of ϵ , the energy which the molecule already possesses, is increased. The chance that a molecule of energy ϵ will acquire the additional energy $\Delta\epsilon$ in a fixed period of time by the absorption of radiant energy depends only on the density of radiation of frequency $\nu = \Delta\epsilon/h$, and on the absorption coefficient of the molecule for radiation of this frequency. The smaller energy difference between quantum states at high energies and the greater *a priori* probability of the higher states indicate that the absorption coefficient for low-frequency radiation may increase rapidly with the energy ϵ of the molecule. This is in accord with the experimentally observed increase in the infra red absorption coefficients of many gases with rise in temperature.

It is probably true, therefore, that as we consider higher and higher steps of energy acquisition the relative importance of the absorption of radiation increases in comparison to the transfer of energy by collisions. However, calculations already made of the rate of activation by radiation, using the absorption coefficient of nitrogen pentoxide, expressly included the possibility of activation by the absorption of low energy radiation by molecules of high energy existing in equilibrium numbers. It would, therefore, be necessary, if this process is to play an important part in the normal mechanism of activation, that these molecules of abnormal energy (but unactivated) possess an enormously higher absorption coefficient than the normal molecule.

In this case the absorption of energy by collisions would be the mechanism of greatest rapidity up to a certain energy above which the activation due to radiation would become the predominant factor in the mechanism of producing activated molecules for the reaction. If such a mechanism were the true one the rate of the reaction could not be even approximately maintained in the absence either of collisions or of radiation. This possibility is in no way inconsistent with experimental facts presented here or elsewhere and should not be neglected in considerations

¹⁷ Rice and Ramsperger, *THIS JOURNAL*, 49, 1617 (1927).

of the possible mechanisms of chemical reaction. Such a mechanism would also show a lowering of the specific reaction rate at low pressures found for some typical unimolecular reactions by Hinshelwood and Thompson,¹⁸ Hinshelwood¹⁹ and Ramsperger,²⁰ and discussed by Rice and Ramsperger¹⁷ in connection with the mechanism of activation.

Acknowledgment should be made to Professor G. N. Lewis at whose suggestion this work was started and whose constant advice and aid made the research possible.

Summary

The absorption coefficient for black body radiation of low temperatures has been measured for nitrogen pentoxide. The values obtained were of sufficient accuracy to determine that the rate of activation of nitrogen pentoxide by radiation alone is of insufficient rapidity to account for the observed decomposition rate.

The racemization of pinene under the influence of radiation in a molecular stream was also studied. Under the conditions of the experiment there were no collisions and the concentration of gas was sufficiently low to avoid decreasing the radiation density by absorption in the outer layer. The concentration of radiation over the greater part of the frequency range was far above that in a hohlraum at a temperature sufficiently high to produce racemization in the time of exposure used in the experiment. No racemization was observed.

Attention was called to the fact that a theory involving both collisions and radiation as necessary for observed rates of activation was conceivable and not incompatible with experimental phenomena, although radiation *alone* could not be important in either of the two reactions studied.

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¹⁸ Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, **113A**, 221 (1926).

¹⁹ Hinshelwood, *ibid.*, **114A**, 84 (1927).

²⁰ Ramsperger, *THIS JOURNAL*, **49**, 912 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. I. THE USE OF THE CHLORANIL ELECTRODE IN GLACIAL ACETIC ACID AND THE STRENGTH OF CERTAIN WEAK BASES

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It is well known that many substances which show no basic properties in water will nevertheless form salts. Thus the salts of various amides, many oxonium salts and the halochromic salts of unsaturated ketones may be prepared from an equivalent quantity of perchloric or sulfuric acid provided certain non-aqueous media are used. In the presence of water, however, such salts are often completely hydrolyzed. In this and the following paper we investigate certain of the properties of these solutions in which salt formation is exceptionally complete, and we propose to call such solutions "superacid solutions." The work of Brönsted¹ has done much to clarify the problem of the interrelations of acids and bases in different solvents, a problem which forms the general subject of the present series of papers, while the behavior of acids in non-aqueous media has been the subject of investigation by Hantzsch,² who has brought to light many important relationships in this field.

We attempted to attack this problem in a quantitative way by investigating the hydrogen-ion activity of various non-aqueous solutions and selected the e.m.f. method as initially the most promising, provided a suitable electrode could be found. If "salt-errors" are to be avoided, an electrode must be used in which the activities of all reacting electrode materials with the exception of the hydrogen ion are the same for all the solvents studied. Such electrodes are the hydrogen electrode, the two *saturated* quinhydrone electrodes of Biilmann³ and the various saturated electrodes investigated by Conant and Fieser,⁴ who studied many substituted quinones. The usefulness of the hydrogen electrode and of certain of the others is limited by the chemical reactivity of their active materials or by the susceptibility of the electrode to the action of "poisons." As a first solvent for investigation we chose acetic acid, because this substance has been repeatedly shown to be suitable for the preparation of salts of very weak bases. In this solvent the most suitable electrode appeared to be that formed by the completely chlorinated quinone (chloranil, tetrachloroquinone) and its hydroquinone. This electrode had already

¹ Brönsted, *THIS JOURNAL*, **49**, 2554 (1927) and previous papers.

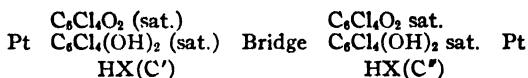
² (a) Hantzsch, *Z. Elektrochem.*, **29**, 221-246 (No. 6, 1923); (b) *Ber.*, **60**, 1933 (1927).

³ Biilmann, *Bull. soc. chim.*, **41**, 213-286 (1927).

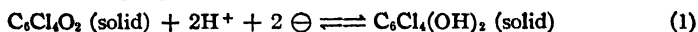
⁴ Conant and Fieser, *THIS JOURNAL*, **45**, 2207 (1923).

been tested in acetic acid solutions in this Laboratory⁵ and found to be satisfactory. Its advantages over other saturated electrodes are (1) chemical inertness and (2) low solubility of the electrode materials.

To illustrate the principle of our method, let us consider the following electrochemical cell



Both electrodes are strictly reversible. When the cell operates, solid chloranil ($\text{C}_6\text{Cl}_4\text{O}_2$) is converted into hydrochloranil at one electrode and the reverse process occurs to the same extent at the other electrode, according to the following equation



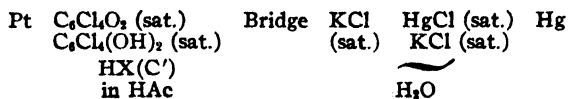
This is obviously independent of the nature of the solutions in the two halves of the cell. If the bridge adequately eliminates the liquid junction potential, the e.m.f. of the cell (E) is a measure of the free-energy change attending the passage of one mole of hydrogen ion from one solution to the other.

E is thus a measure of the difference in the partial molal free energy of the hydrogen ion in the two solutions or of the difference of the logarithms of the corresponding hydrogen-ion activities, thus

$$\frac{\bar{F}''}{F} = \frac{RT}{F} \ln \left(\frac{a' \text{H}^+}{a'' \text{H}^+} \right) \quad (2)$$

If such a cell is to be used to determine the hydrogen-ion activity of one of the solutions, that of the other must be fixed by reference to some standard state. There are a variety of possible ways of selecting the standard state. It has seemed most desirable to us to choose for each solvent a particular solution of which the electrically measured hydrogen-ion activity is set equal to unity. This we have done for acetic acid as later described (p. 3059). Essentially the same thing has been done for water by assigning the single potential $E = 0$ to the "normal" hydrogen electrode.

To increase the reproducibility of our measurements we found it desirable to compare different acetic acid solutions, not directly with each other, but each separately with a standard aqueous reference electrode. In other words, we measured the e.m.f. of cells of the following type



regarding their potentials as positive when the platinum electrode was positive to the mercury.

⁵ Conant, Small and Taylor, *THIS JOURNAL*, 47, 1959 (1925).

In our work, the siphons of the calomel half cells, which terminated in glass stoppers, usually dipped into a beaker of saturated potassium chloride solution, into which also dipped one end of the special bridge which is later discussed in detail. This was a glass-stoppered U-tube containing a concentrated acetic acid solution of lithium chloride and gelatin. The other end of the bridge dipped into another beaker which contained the solution under investigation (saturated with chloranil and hydrochloranil), the platinum electrodes and an electrically driven stirrer. The e.m.f. of the cell was compensated and measured by means of a potentiometer, with the aid of a quadrant electrometer as null instrument.

The first and most striking of the early results of our work was the large e.m.f. of cells of the type just described when the acetic acid solution contained considerable concentrations of strong acids. For example, a chloranil electrode in a 0.064 *M* solution of sulfuric acid in acetic acid is 0.735 volt more positive than the saturated calomel electrode, when the measurement is made as just described. The corresponding figure for 1 *M* sulfuric acid is +0.756 volt, and for 1 *M* perchloric acid about +0.83 volt. A 1 *M* solution of trichloro-acetic acid gave a potential of only +0.615. These high potentials were reduced in an orderly manner whenever basic substances such as pyridine, urea or sodium acetate were added to the solution, and this fact permitted the *titration* of the various acids with bases, and of the bases with acids. Good titration curves were obtained in numerous instances, as is shown below (Figs. 1 and 3) in the case of bases. *The process of salt formation could thus be studied in as satisfactory a way as in water, by the aid of these titration curves. Indeed it was even possible to titrate such bases as acetamide, benzamide, and acetanilide, which cannot be titrated in water solution.* The titration and relative strengths of acids will be discussed in a later communication.

Apparatus and Materials

Platinum Electrodes.—Two or more electrodes of blank platinum foil or wire were used in each measurement. Foils of a considerable size (10 × 15 mm.) appeared to be most satisfactory. The electrodes were usually cleaned by scrubbing with sand, ignited and allowed to stand in a solution containing the chloranil mixture and some buffer mixture of a not too acid character. After ignition, or prolonged standing in the air, or washing with water, the electrodes often required a considerable time (fifteen to twenty minutes) to attain their equilibrium potentials. If, after use in one solution, they were simply washed in glacial acetic acid and placed in another, their subsequent recovery was much quicker, and if they were merely transferred from one glacial acetic acid mixture containing chloranil to another, the final potential was attained as rapidly as the solution could be completely mixed. This last point was important in titrations, where apparently with sufficiently vigorous stirring there was no lag whatever unless some slow reaction was taking place in the solution.

The criteria by which electrodes were judged were as follows: (1) agreement between many electrodes in the same solution; (2) rapid attainment of final potential; (3) rapid and complete recovery after polarization (in the earlier work with a low re-

sistance circuit); (4) attainment of a particular potential in a particular buffer (in the later work). In general, new electrodes satisfied these criteria very well and often could be used for weeks in solutions of low acidity without exhibiting any indication of poisoning. Agreement of four electrodes within one millivolt was frequently attained and on certain occasions within 0.2 millivolt.

On the other hand, in solutions containing high concentrations of acetic anhydride, perchloric acid, fuming sulfuric acid or even of ordinary sulfuric acid, the agreement between different electrodes was sometimes much less satisfactory, and certain ones exhibited a tendency to give divergent values (generally less positive than the average). After repeated use in such solutions these divergencies sometimes became very large (0.1 to 0.2 volt) so that the electrodes were completely useless. It was remarked that when an electrode gave values say 50 millivolts low in the most acid solutions, it generally gave values about 5 millivolts low in the ordinary solutions. Ignition, scouring and scraping were in some cases effective in restoring the original character to the electrode; at other times the poisoned character persisted. On prolonged standing in the air (several weeks) with subsequent ignition, almost all the poisoned electrodes recovered completely. After it was established that a certain buffer containing urea and sulfuric acid showed a definite potential difference against the saturated calomel half-cell, it was possible to test electrodes by their performances in this mixture, and this was done repeatedly in the later work.

Saturation of the Electrode and the Chemical Activity of Chloranil

Theoretically, the peculiar usefulness of the chloranil electrode depends upon the solution being really in equilibrium at all times with both the solid quinone and its hydroquinone. Therefore, although for many practical purposes such as titrations, considerable variation from the equilibrium conditions seemed to introduce no appreciable error, for the final measurements some pains were taken to devise a technique which at least would insure thoroughly comparable conditions in different experiments. It was found that if a large excess of both solid phases was stirred with the solution at the working temperature, the electrodes very quickly took up a potential which was near, but in general not identical with, the equilibrium potential, and the latter was only reached after a considerable time, sometimes as long as thirty to forty minutes. It therefore seemed best to warm the solvent with an excess of the solids. On cooling, both substances readily crystallized providing the supersaturation had been sufficient, and in five to ten minutes after cooling to room temperature, the equilibrium value of the potential was reached. If now to such a solution which is exactly saturated, a certain volume of titrating solution is added, obviously an at least momentary unsaturation will be introduced. With this in view, it was at first our practice previously to saturate the titrating solution also with both solids. Later we abandoned this practice, having convinced ourselves that no measurable error was introduced by so doing provided the relative volume of the solution added was small. This is to be expected if the solutions approach ideality, unless differences in the *solution rate* of the two solids introduce errors.

In order to save material, we ascertained by preliminary experiments how much of each solid was necessary to give a quick crystallization when the solution was vigorously shaken with the solids for about thirty seconds at a temperature not over 50°, and then cooled under the tap to 25°, the working temperature. The amounts added were always 0.8 g. of tetrachloro-hydroquinone and 0.6 g. of tetrachloroquinone per 100 cc. of acetic acid solution. No effect of a three- or four-fold excess over these amounts was observed. Whenever possible, the acetic acid alone was warmed with the solids and the solutes were added later, just before the final cooling was complete. No error was

introduced, however, in the majority of cases, when the various buffer solutions were themselves warmed with the chloranil. It was also found that solutions of urea and of sulfuric acid saturated with chloranil could be stored for a considerable time without altering in titer or other properties. Pyridine under such conditions developed a cherry red color, while bases of a more actively reducing character rapidly developed various vivid colors and clearly underwent rapid decomposition. We finally avoided storing any of the substances in contact with chloranil, but instead always saturated the portion to be measured or titrated immediately before use, as just described.

Reference Electrodes

The saturated aqueous calomel half-cell was used as a reference electrode. Several of these were prepared and frequently checked. They always agreed within one millivolt with each other and with similar electrodes prepared by other workers. Their siphons dipped either into a beaker of saturated potassium chloride solution, or for special purposes directly into the solution to be measured. In the latter case the end of the siphon was always stoppered with glass.

Salt Bridge

The liquid used as a salt bridge was a supersaturated solution of lithium chloride in acetic acid, which was prevented from crystallizing by dissolving a small amount of gelatin in the acetic acid. The concentration of the two solutes was varied within wide limits without apparent effect on the performance of the bridge. This solution was enclosed in a glass-stoppered U-tube about 35 cm. long and whose internal diameter was about 4 mm.

Measuring Instruments

At first a simple galvanometer was used as a null point indicator in connection with a Leeds and Northrup Type K potentiometer. Later when the lithium chloride bridge was used the resistance of the system became too great for this apparatus and a quadrant electrometer of the Compton type was substituted for the galvanometer. The needle was charged to a constant potential between 67.5 and 180 volts by a "B" battery. One pair of quadrants was permanently earthed, and the other could be connected either to earth or to the system comprising the potentiometer and the cell to be measured. The polarity of the cell could be reversed at will, while the negative side of the potentiometer was permanently earthed. The high-potential part of the system was very carefully insulated and the entire apparatus protected by an earthed shield. The functioning of the electrometer was very satisfactory and its sensitivity was high (up to 25 mm. of scale per millivolt). (The lamp and scale were about 2.5 meters from the mirror.) Its insensitiveness to abuse in the form of large accidental voltages, and its complete prevention of polarizing currents in the system, are advantageous. It also permitted the use of the clean and convenient but high-resistance ground-glass junctions. Serious difficulty was occasionally encountered in adjusting the electrometer to a high sensitivity. The method described by Compton and Compton⁶ was found useful when simple trial and error failed to secure a satisfactory setting. There was also a slow but capricious drift of the zero point, so that a scale with a widely movable zero was a great convenience.

Materials Used

Our principal object was to develop a method of medium accuracy which could be easily applied by others, and to make a rapid exploration of a wide field, rather than

⁶ Compton and Compton, *Phys. Rev.*, 14, 85 (1919).

to obtain data of high accuracy. We, therefore, whenever possible, used materials of commercial grade, but of definite and reproducible character, instead of subjecting our substances to careful purification.

Acetic Acid.—In all of the work described in this paper, a single grade of glacial acetic acid was used, the P. W. R. analytical reagent. This was supposed to contain "at least 99.5% acetic acid." No attempt was made to free it from water or other impurities. In many preliminary experiments the ordinary "U. S. P. 99.5%" grade purchased in carboys was used and no difference in behavior was detected. In making up the solutions described in the following paper, still another grade of analyzed acid was employed, but no difference in behavior was found.

Tetrachloroquinone (chloranil).—This was the Eastman Kodak Company's "No. 603 MP 283-284°." Recrystallization from acetic acid had no effect on its electrochemical behavior and was generally omitted.

Tetrachlorohydroquinone.—This was prepared from the previous material substantially as described by Conant and Fieser,⁴ except that it was not precipitated by alcohol from glacial acetic acid solution. When thoroughly purified it melted very sharply at 236-237°, but certain samples of lower melting point showed identical electromotive behavior.

Perchloric Acid.—The 60 per cent. aqueous solution was added slowly to five times its volume of chilled acetic anhydride reagent and further diluted to the desired volume with acetic acid. The resulting solution was then titrated against a urea, pyridine or sodium acetate solution of known concentration.

Other Materials.—The other acids and bases used were of the best c. p. grade ordinarily obtainable.

Experimental Results

Titration of Bases.—Fig. 1 shows the potentials (E) obtained when small volumes of 2 M sulfuric acid were added to large volumes of solutions of the various bases, at such concentration that they were 0.2 M in total base at the mid-point of neutralization. The temperature was $25 \pm 0.5^\circ$. The solutions were all prepared and saturated in the same way and the potentials measured against the saturated calomel half-cell, through the lithium chloride bridge, with the quadrant electrometer. The choice of substances was such as to give as wide a range of base strength as possible. Thus acetanilide, at the top of the diagram, is a very weak base indeed. Passing through progressively stronger bases, one notes the appearance of a slight inflection with urea, and this becomes steadily more marked as the strong bases are reached. A double bend is shown by the two strongest bases, *p*-toluidine and pyridine, which is due to the successive action of the two hydrogens of the sulfuric acid molecule. It will be noted that two bases which do not contain nitrogen are included, the two xanthydrols. It was necessary to titrate these in more dilute solution (0.05 M and 0.04 M) on account of their low solubility. The relative position of the curves is reliable to about 0.010 volt at least.

In Fig. 2 the logarithm of R , the ratio of salt to free base, is plotted against the e.m.f. data of Fig. 1. The numbering of the curves is the same in the two figures. "One hundred per cent. neutralized" means 1

mole of sulfuric acid per mole of base. If the curves of Fig. 1 had exactly the theoretical shape, the points for each substance would fall on a straight line in Fig. 2 and the slope of these lines would be

$$\frac{\Delta \log R}{\Delta E} = \frac{1}{.0591}$$

as shown by the lines marked "theoretical slope."⁷ Departure from these conditions must be due to changes in the activity coefficients of various

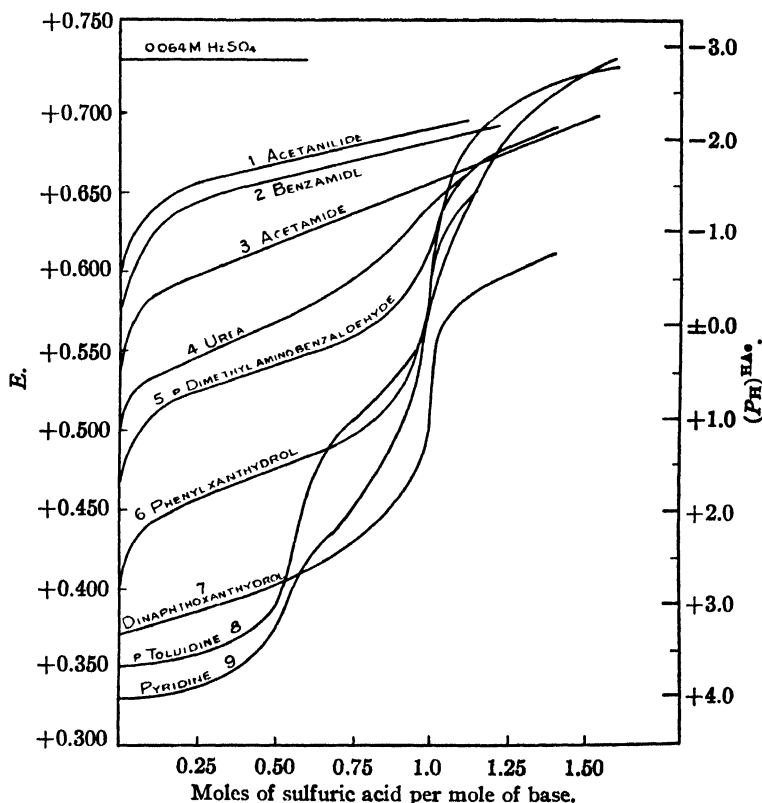


Fig. 1.—Titration curves of bases with sulfuric acid in glacial acetic acid (mono-amines and carbinols).

molecular species concerned in the equilibria, or to changes in the liquid junction potential. That these departures are no greater, especially in the less acid solutions, is fortunate, and perhaps surprising.

Polyamines

None of the substances in Fig. 1 adds more than one hydrogen ion per molecule. Fig. 3 shows the titration curves of four polyamines, each of

⁷ For convenience in studying the diagram, percentage neutralizations are shown at the left, as well as the corresponding values of the true ordinate ($\log R$) at the right.

which shows distinctive behavior. These curves were obtained under the same conditions as those of Fig. 1. It will be noted that substance No. 1, Michler's ketone, tetramethyldiaminobenzophenone (4,4'), shows scarcely a trace of inflection until two moles of acid have been added. Hexamethylenetetramine shows a sharp inflection when only one-half mole of acid has been added per mole of base. This must represent the formation of the salt $(RN_4H)_2^+(SO_4)^-$. This point once passed, a heavy white precipitate appears in the solution, which acts as a very efficient buffer, the potential remaining constant while 0.8 mole of acid is being added per mole

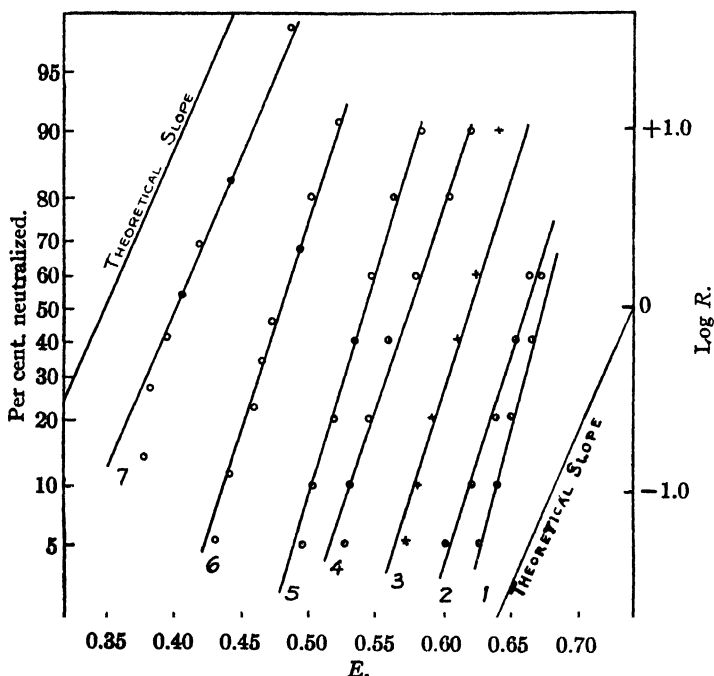


Fig. 2.—Logarithmic titration curves of bases in acetic acid.

of base originally present. Then once more a break occurs, steeper this time, corresponding to the complete formation of $(RN_4H_2)^{++}(HSO_4)_2^-$ or of $(RN_4H_4)^{++++}(SO_4)_2^{--}$. The addition of acid was continued until four moles of sulfuric acid were present per mole of base, but no additional inflection was noted.

No. 3, hydrobenzamide, shows a slight, but distinct, inflection at one mole of acid $[(RN_2H)^+(HSO_4)^- \text{ or } (RN_2H_2)^{++}(SO_4)^-]$ and a much sharper one at two moles. The substance smelled strongly of benzaldehyde, indicating partial decomposition.

No. 4, *p*-phenylenediamine, formed dark-colored solutions, indicating oxidation by the chloranil, and at least one substance was precipitated

in the course of the titration. Nevertheless, it seemed worth while to exhibit its striking curve

The data of Figs. 1, 2 and 3 demonstrate the existence in acetic acid solutions of a system of acids and bases quite similar to the familiar water system, and show that this system may be explored with the aid of the chloranil electrode.

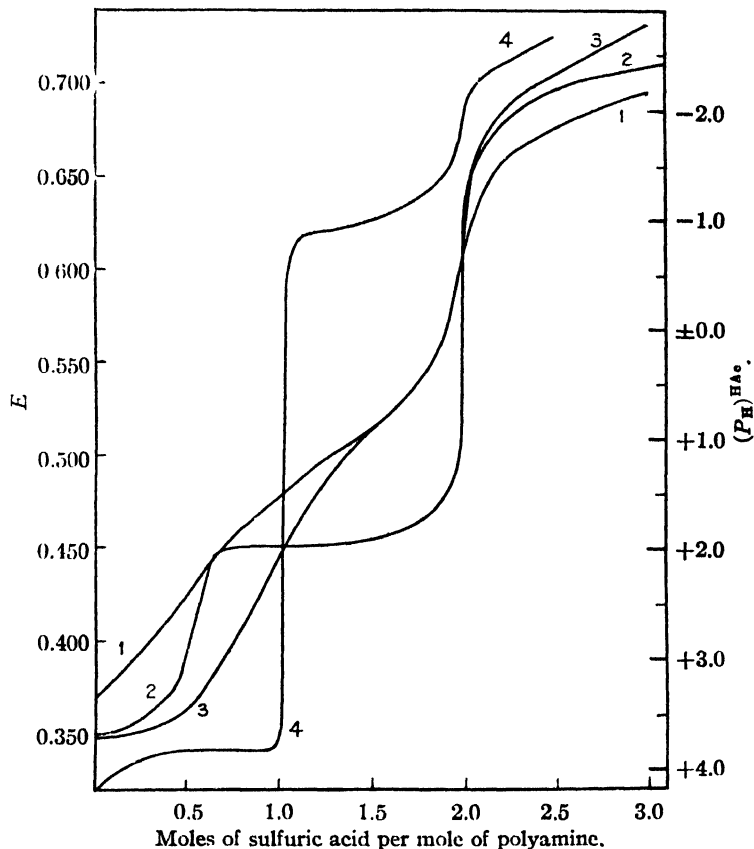


Fig. 3. —Titration curves of polyamines with sulfuric acid in glacial acetic acid. 1. Michler's ketone; 2. hexamethylene tetramine; 3. hydrobenzamide; 4. *p*-phenylenediamine.

Effect of Water and Alcohol on the Potentials

It seemed interesting to determine the effect on the potentials of our solutions of adding small amounts of water or alcohol. The results of such an inquiry are summarized in Fig. 4. The abscissas are percentages of water or alcohol; the left-hand scale of ordinates, potentials measured in the usual way. The measurements were obtained as follows. (1) (Top curve). An acetic acid solution 0.2 *M* in perchloric acid, half neu-

tralized with urea (and containing some acetic anhydride), was prepared and saturated with chloranil mixture. It was 0.802 volt more positive than the calomel electrode. Small amounts of absolute alcohol were then added until the total alcohol content of the solution reached 70% by volume. The potential had now fallen to +0.525 volt. The other solutions studied were 0.2 *M* sulfuric acid half neutralized with urea and 0.2

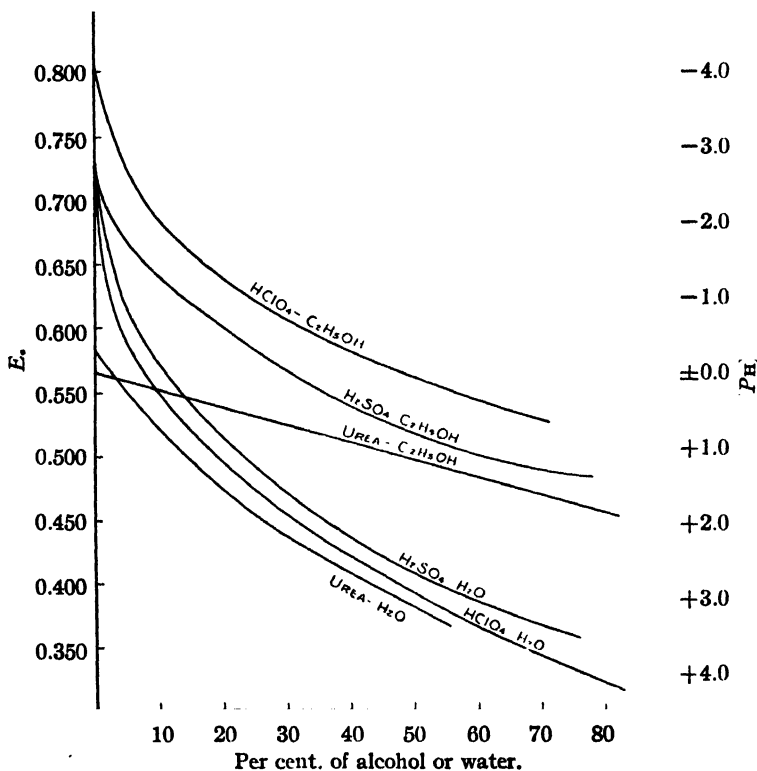


Fig. 4.—Effect of alcohol and water on potentials of buffer mixtures in glacial acetic acid. The first formula or name on each curve gives the principal solute, which is in each case half neutralized with urea (or sulfuric acid), and at an initial concentration of 0.2 *M*.

M urea half-neutralized with sulfuric acid. To each of these three, water and alcohol were separately added. The effect of water was much the greater, particularly at the beginning of the curve. The exact course of the curves is doubtless affected by changing liquid junction potentials. These data show clearly that a variation in the water content of the acetic acid of the order of one per cent. is not serious in the urea solutions but becomes very important as the highest acidities are reached. A few scattered experiments indicated that the addition even of small amounts

of acetic anhydride produced a slight but significant increase in the potentials, particularly in the most acid solutions.

Effect of Concentration and of Various Ions

In order to limit as far as possible the number of variables in our preliminary work, we made our final comparisons all at the same concentration and with no other anions present than those furnished by sulfuric acid. The concentration chosen, largely for convenience and to secure good buffer capacity, was 0.2 *M*. A few preliminary tests indicated that between 0.1 *M* and 0.4 *M* the effect of change of concentration was slight. At concentrations below 0.1 *M* rather large variations were encountered. We have reserved for a later paper the question whether these are due to activity changes incident to changes in the ionic strength of the solutions or to changes in the liquid junction potentials. Preliminary calculations support the former view.

In general, when a base was titrated with perchloric acid rather than with sulfuric, the corresponding potentials were slightly higher. The presence of acetic anhydride in the perchloric acid solutions, coupled with the extreme water-sensitivity of their potentials, makes it difficult to be certain whether this effect is really due to a difference in anion or to a difference in the effective water content of the solutions. This point also will form the subject of later work.

Discussion of Results

The Magnitude of the Potentials and the Use of the Lithium Chloride Bridge

The high values of the potentials, especially in the most acid solutions (see p. 3049), raise the question of the extent to which they are affected by the unknown liquid junction potentials in the cell. It also remains to justify the use of the lithium chloride bridge in all our final measurements. A salt bridge in measurements of this kind may be said to have three functions.

- (1). To promote the reproducibility of the measurements.
- (2). To neutralize the effect of varying liquid junction potential between the different acetic acid solutions.
- (3). To eliminate if possible the potential at the junctions between the saturated aqueous potassium chloride and the various acetic acid solutions, or at least to promote its constancy.

(1). When two acetic acid solutions were directly joined through a porous cup or a ground-glass stopper, it was found that their difference of potential generally, but not always, had the same value within 0.005 volt. When these solutions were then each separately measured against a third solution, the difference of the potentials thus obtained often varied

from the "direct" value by $\pm .015$ volt or more. A number of solutions were tried as "reference electrodes" but in no case was the system of potentials measured against a wide variety of other solutions completely self-consistent. As it seemed that part of the difficulty might lie in the non-reproducibility of the various acetic acid chloranil half-cells, we next prepared a number of (aqueous) saturated calomel half-cells, whose siphons were stoppered rather tightly at the end with glass stoppers.

These stoppered ends, which thus formed potassium chloride bridges of a fairly reproducible type, were allowed to dip directly into the various acetic acid solutions and the measurements thus all referred to the saturated calomel half-cell. Under these conditions, reproducible values (within .005 volt) were nearly always obtained *except in the more acid solutions*, where gross discrepancies of the order of .04 volt made their appearance.

It now occurred to us to interpose, between the highly acid solutions and the saturated aqueous potassium chloride, another acetic acid solution, substantially "neutral" (in the acetic acid system), and containing a high concentration of some electrolyte. Lithium chloride seemed to be the best salt for our purpose.

In order to increase the available concentration range, we prepared supersaturated solutions which we prevented from crystallizing with the aid of gelatin. These solutions were enclosed in a U-tube with well ground stoppers, and the ends of this tube dipped, respectively, into the acetic acid solutions and into saturated potassium chloride connected with the calomel electrode.

With this experimental arrangement the reproducibility of all the measurements, even in the more acid solutions, appeared satisfactory for our purpose. The discrepancies were rarely as great as 0.005 volt.

(2). The self-consistency of the measurements made with the aid of the lithium chloride bridge, and the approximation of the lines of Fig. 2 to the theoretical slope, seem to indicate that there are no errors due to liquid junction potentials between the different acetic acid solutions, of a much higher order of magnitude than the extreme variation of the individual measurements (0.005 volt).

(3). The question of the magnitude of the junction potential between the saturated potassium chloride solution of the calomel electrode and the various acetic acid solutions through the lithium chloride bridge is much more uncertain. A small amount of evidence, as yet of a very uncertain character, leads us to believe that this potential is of the order of 0.15 volt, and of such sign as to increase the apparent e.m.f. of the cells. In preliminary work of this character the *magnitude* of such a potential is of much less importance than its *constancy*. The reproducibility and self-consistency of all our measurements in acetic acid seem to be evidence that the junction potential is effectively constant.

As they stand, our e.m.f. measurements give a direct measure of the hydrogen-ion activity of the acetic acid solutions, relatively to each other. As it is customary, however, in dealing with aqueous solutions, to think of hydrogen-ion activity in terms of " P_H units" (1 P_H unit = .0591 volt at 25°) instead of in volts, it has seemed desirable to employ a similar unit in discussing our results in glacial acetic acid. We have, therefore, adopted the symbol $(P_H)^{HAc}$ as a convenient designation for our purpose.

We are then confronted with the necessity of selecting a zero for the scale thus constituted. If it could be assumed that the liquid junction potential between water and acetic acid solutions was *eliminated* by the bridge in our measurements, it would be rational to choose as zero a potential of +0.418 volt against the calomel electrode, as this is the normal potential of the chloranil electrode when so measured in aqueous solution.⁴ Since we have no assurance that our liquid junction potential is negligible, we have arbitrarily taken the zero of our scale to correspond to a potential of 0.566 volt.⁸ This means merely that we have decided to call unity, for our present purposes, the hydrogen-ion activity of a solution in which the chloranil electrode has the stated potential (+0.566 volt) measured as above described.

The measured potentials (E) and the $(P_H)^{HAc}$ values are thus related as follows

$$(P_H)^{HAc} = \frac{0.566 - E}{0.0591} \text{ at } 25^\circ$$

We have inserted in our diagrams as alternative ordinates the $(P_H)^{HAc}$ values as thus defined. It will be noted that many of these values are negative, because of the high acidity of some of our solutions. In terms of the new unit, the acidities of the solutions mentioned on p. 3049 are as follows

TABLE I
ACIDITIES OF SOLUTIONS

Solution	E (volts)	$(P_H)^{HAc}$
1.0 M Cl_3CCO_2H	+0.615	-0.83
1.0 M H_2SO_4	+0.766	-3.23
1.0 M $HClO_4$	+0.83	-4.4

⁸ It is our hope that the zero point of this arbitrary scale will be shown eventually to be very near the zero point of the P_H scale in water. The two chief reasons which have led us to adopt tentatively this particular standard are as follows. (1) It seems probable that the strength of anhydro bases should be approximately the same in different solvents, and this is the case for urea, dimethylpyrone and acetamide in acetic acid and water as we have defined the $(P_H)^{HAc}$ scale (see Table II). (2) The solvent (acetic acid) half neutralized with a relatively strong base such as pyridine might be expected to have a hydrogen-ion activity of the same order of magnitude as the pK_A of acetic acid dissolved in water. The $(P_H)^{HAc}$ of an equimolar mixture of pyridine and pyridine acetate is about +4.4 as compared to the value +4.7 given for the pK_A of acetic acid in water.

Relative Strength of Bases

As a matter of interest we now present a list of numbers (Table II) intended to represent as closely as possible the relative strength of all the bases we have been able to titrate accurately, in the absence of complications such as the appearance of precipitates. This list includes not only most of the bases of Figs. 1 and 3, but also several others for which the measurements, for lack of space, are not reported in detail. In this table we designate by $(pK_A)^{HAc}$ the $(P_H)^{HAc}$ value of a 0.2 *M* solution of each base half neutralized with sulfuric acid. These $(pK_A)^{HAc}$ values should be more or less closely related to the negative logarithms of the hydrolysis constants of strong-acid salts of the base in water solution.

$$pK_B^{H_2O} = -\log K_B^{H_2O}, K_B^{H_2O} = \frac{10^{-14}}{K_B^{H_2O}}$$

where $K_B^{H_2O}$ is the ordinary dissociation constant of the base. Where they are known, values of $pK_B^{H_2O}$ at 25° are given for comparison.

Most of the water values are taken from Landolt-Börnstein's "Tabellen." The figures for *p*-toluidine and triethylamine are from unpublished measurements by one of us. The essential identity of behavior in acetic acid shown

TABLE II
RELATIVE STRENGTH OF BASES IN ACETIC ACID SOLUTION

Substance	$(pK_A)^{HAc}$	$(pK_B)^{H_2O}$
Triphenylcarbinol	Too weak to measure	Too weak to measure
Triphenylamine		
2,4-Dinitroaniline		
Acetanilide	-1.75	Too weak to measure
N- <i>p</i> -methylbenzyl formamide	about -1.65	Too weak to measure
N- <i>p</i> -methylbenzyl acetamide		
N- <i>p</i> -methylbenzyl butyramide		
Benzamide	-1.60	Too weak to measure
Acetamide	-0.9	-0.5
Urea	-0.05	+0.18
Dimethylpyrone	about 0.0	+0.3
Diphenylamine		?
<i>p</i> -Nitro-aniline		+2.0 (?)
<i>p</i> -Dimethylaminobenzaldehyde	+0.4	?
Michler's ketone (2nd stage)	+1.0	?
Hydrobenzamide (2nd stage)	+1.0	?
Phenylxanthidrol	+1.5	?
Michler's ketone (1st stage)	+2.5	?
Dinaphthoxanthidrol	+2.65	?
"Nitron"	strong	?
<i>p</i> -Toluidine	strong	+5.11
Pyridine	strong	+5.36
Triethylamine	strong	+10.75

NOTE: In the case of the methyl benzyl amides, the measured values have been increased by 0.1 unit to allow for differences in the concentration of their solutions from the standard concentration.

by urea and *p*-nitro-aniline leads us to believe that a redetermination of the constant of the latter substance in water is desirable.

It is necessary to add that while the picture of relative base strength thus presented is undoubtedly correct in its main outlines, the possibility remains that the zero of our scale is improperly placed by as much as one or two units and that the "constants" we have given would be modified in the presence of water, acetic anhydride or other substances, or by changes in concentration.

It is perhaps entertaining at this point to pursue somewhat further the implications of our choice of zero for the acetic acid scale. If, as we hope, we have estimated the junction potential between acetic acid and aqueous solutions with approximate correctness, then our $(P_H)^{HAc}$ values become approximate measures of the hydrogen-ion activity of the various solutions referred to the water standard. The hydrogen-ion activities (or activity coefficients, since we are dealing with unit concentrations) of the three solutions listed in Table I, are then respectively 6.7, 700, and 25,000. That such high activities are possible, even in water solutions, is indicated by the work of Lewis and Randall⁹ on concentrated HCl solutions. Their most acid solution (16 molal hydrochloric acid) showed a mean ionic activity coefficient of 43.2, or a mean ionic activity of 691, which compares favorably with the values for our (much less concentrated) solutions in acetic acid. The " P_H value" of such a solution is -2.84 on the assumption that the two individual ion activities are equal. The true value is doubtless still more negative. We feel that our work indicates that the proximate cause of superacidity in a solution is an abnormally high value of the hydrogen-ion activity. An hypothesis to account for this phenomenon is tentatively proposed in the following paper.

We take pleasure in expressing our thanks to Mr. Edwin B. Damon, who kindly gave us the benefit of his experience with quadrant electrometers.

Summary

1. A method has been developed in which the chloranil electrode is used to measure hydrogen-ion activities in glacial acetic acid solutions.
2. The reliability and significance of such measurements are discussed.
3. Titration curves are given for several bases in this solvent and their significance noted.
4. The bases studied are arranged in order of increasing strength and characterized by a set of constants allied to the hydrolysis constants of their salts in water solution.

CAMBRIDGE 38, MASSACHUSETTS

⁹ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 336.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. II. A CHEMICAL INVESTIGATION OF THE HYDROGEN-ION ACTIVITY OF ACETIC ACID SOLUTIONS

BY JAMES B. CONANT AND NORRIS F. HALL

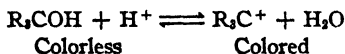
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The preceding paper of this series has demonstrated that the hydrogen-ion activity of glacial acetic acid solutions may be estimated by means of the chloranil electrode. In this paper we shall show that the halochromism of triarylcarbinols, the halochromism of unsaturated ketones and the rate of inversion of cane sugar are controlled by the hydrogen-ion activity as measured electrochemically. The general agreement between the four independent methods seems to us to establish beyond doubt the possibility of measuring in this solvent hydrogen-ion activities which have the same general significance as those measured in water.

The Halochromism of Arylcarbinols and Unsaturated Ketones

Triarylcarbinols such as triphenylcarbinol and certain diarylcarbinols give intensely colored salts when treated with acid in suitable media. Some of the derivatives of triphenylcarbinol which contain a number of methoxy groups form halochromic salts even in aqueous solutions. A careful quantitative study of these compounds has recently been made by Lund¹ and by Kolthoff² who have shown that they may be used as indicators in aqueous and alcoholic solutions. From this work of Lund and from that of Hantzsch³ it seems quite clear that the triarylcarbinols are pseudo bases of varying strength. Indeed this was essentially Baeyer's original idea. The equilibrium involved in the formation of the colored ion may be represented as follows



If we use a medium in which the carbinol and salt are both soluble, the appearance of color will be a function both of the hydrogen-ion activity and the water activity. If the latter is constant in a series of solutions the appearance of color may be used as a method of estimating the hydrogen-ion activity.

Unsaturated ketones such as benzalacetophenone ($\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$) also give intense colors with concentrated mineral acids. Hantzsch⁴ be-

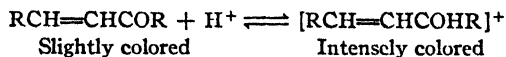
¹ Lund, *THIS JOURNAL*, **49**, 1346-1360 (1927).

² Kolthoff, *ibid.*, **49**, 1218-1221 (1927).

³ Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); *Ber.*, **55**, 953 (1922).

⁴ Hantzsch, *Ref. 2* and *Zeit. Elektrochemie* No. 6 (1923) in which the use of di-benzalacetone as an indicator is discussed.

lieves this to be also an example of salt formation and we may write the equilibrium



The unsaturated ketones are thus anhydro bases which form a colored ion. They would be expected to differ from the carbinols only in that the appearance of color is a function solely of the hydrogen-ion activity; the activity of the water *per se* should not affect the composition of the equilibrium mixture.

In order to investigate the halochromism of a number of carbinols and unsaturated ketones we prepared a series of acetic acid solutions of graded hydrogen-ion activity and with a constant and small water content. With the exception of the two most acidic they were mixtures of sulfuric acid and very weak bases dissolved in acetic acid. Thus, they were "buffered" in respect to both the increase and decrease of hydrogen-ion activity.

The results are summarized in Table I, which is self-explanatory. The data are remarkably consistent with each other and with the e.m.f. measurements. It seems certain from these more than 100 experiments that the halochromism of both the carbinols and the unsaturated ketones is determined within at least 0.5 of a $(P_H)^{\text{HAc}}$ unit by the hydrogen-ion activity of the solution as found from e.m.f. measurements.

A further test of the general consistency of the results is made possible by the fact that the titration curves of a number of the very weak bases lie close together (Fig. 1, preceding paper). Since this is the case it should be possible to titrate with an indicator a given weak base with sulfuric acid to the same color as that shown by the same indicator in one of the buffered solutions. The result should agree with the e.m.f. titration data. Thus, the acetamide buffer (No. 5, $(P_H)^{\text{HAc}} = -1.0$) was used as a standard, and benzamide was titrated with sulfuric acid, using indicator F' in both the standard and the titrating solution. The same relative concentration of indicator was used and the same concentration of base (0.2 M). A color match was obtained when 0.1 cc. of M sulfuric acid was added (1 cc. required for total neutralization); from the e.m.f. titration curve the calculated quantity for $(P_H)^{\text{HAc}} = -1.0$ would be 0.1 cc. The other results were as follows: Urea titrated to match $(P_H)^{\text{HAc}} = -1.0$ (indicator F') required 0.9 cc., calcd. 0.9 cc.; acetamide to match $(P_H)^{\text{HAc}} = -0.5$ (indicator F') required 0.2 cc., calcd. 0.2 cc.; benzamide to match $(P_H)^{\text{HAc}} = -2.0$ (acetanilide buffer) (indicator C) required 1.4, calcd. 0.9; titrating acetanilide to match $(P_H)^{\text{HAc}} = -1.5$ (benzamide buffer) with indicator D' required 0.1 cc., calculated 0.2 cc.

The differences between the required and the calculated amount of acid in titrating acetanilide or comparing benzamide with the acetanilide buffer amount to 0.3 of a $(P_H)^{\text{HAc}}$ unit. This is an indication of the magni-

TABLE I
TURNING RANGE OF UNSATURATED KETONE AND CARBINOL INDICATORS IN GLACIAL ACETIC ACID SOLUTION*

	Buffer solution	(P_H) _{HAo} predicted from com- position	(P_H) _{HAo} measured directly	A'	B	C	D'	Indicator (see below)	E'	G'	H'	I	J
1	1.0 M H ₂ SO ₄	-2.7	-3.22	+	+	+	+	+	+	+	+	+	+
2	0.064 M H ₂ SO ₄		-2.78	-	+	+	+	+	+	+	+	+	+
3	Acetanilide 0.76 neutral- ized	-2.0	-2.03	-	+	+	+	+	+	+	+	+	+
4	Benzamide 0.40 neutral- ized	-1.5	-1.5	-	-	-	-	(+ -)	+	+	+	+	+
5	Acetamide 0.55 neutralized	-1.0	-1.0	-	-	-	-	-	+	+	+	+	+
6	Urea 0.75 neutralized	-0.5	-0.55	-	-	-	-	-	+	+	+	+	+
7	Urea 0.44 neutralized	-0.0	-0.0	-	-	-	-	-	+	+	+	+	+
8	Urea 0.14 neutralized	+0.5	+0.42	-	-	-	-	-	-	-	-	+	+
9	Hexamethylenetetramine 1.20 neutralized	+2.05	+1.99	-	-	-	-	-	-	-	-	-	+
10	Hydrobenzamide 0.85 neutralized	+2.5	+2.85	-	-	-	-	-	-	-	-	-	+
11	Hexamethylenetetramine 0.15 neutralized	+3.6	+3.62	-	-	-	-	-	-	-	-	-	-

* Col. 1. Each buffer, except the first two, contained the base named in 0.2 M concentration, dissolved in glacial acetic acid. To this had been added sufficient sulfuric acid to neutralize the stated fraction of the base, on the assumption that one mole of the base was neutralized by one mole of acid. The acetic acid was "P. W. R. analytical, complying with dichromate test." The sulfuric acid was "P. W. R. analytical 94 to 97%." It was assumed to contain 95% H₂SO₄. The acetanilide showed an extremely faint brownish color. The benzamide left a very slight white residue on dissolving. The hexamethylenetetramine "1.20 neutralized" contained a large amount of white precipitate (sulfate or hydrosulfate). The hydrobenzamide developed a pronounced yellow color on standing, smelt of benzaldehyde, and formed a slight precipitate when treated with sulfuric acid. The other solutions were clear and colorless.

Col. 2. The "(P_H)_{HAo} predicted" was read from titration curves previously obtained (see Fig. 1 preceding paper).

Col. 3. The "(P_H)_{HAo} of each solution was measured directly with the technique previously described (p. 3049 preceding paper). The benzamide values showed a slight drift with time, a phenomenon previously observed. Acetanilide, whether alone or in the presence of sulfuric acid, gives an orange color with chloranil.

Indicators. These were unsaturated ketones (denoted by "primed" letters) or substituted carbinols. They were all 0.05 *M* in glacial acetic acid as a solvent. The meaning of the signs used is as follows: +, halochromic color; ++, +++, +++++, etc., very intense color; -, no halochromic color; +-, transitional color; (+-), doubtful color.

The comparison was carried out by adding the stated number of drops to 5 cc. of each buffer. The tubes were shaken slightly to mix the solutions.

A' Benzalacetophenone. 10 drops. Buffer No. 1, pale yellow; all others colorless.

B Triphenylcarbinol. 10 drops. No. 1, full yellow; 2 and 3, pale yellow; all others colorless.

C Diphenyl- α -naphthylcarbinol, 5 drops. No. 1, inky greenish-blue; 2 and 3, clear greenish blue. All others colorless.

D' Piperonalacetophenone. 8 drops. No. 1, red-orange; 2 and 3, strong yellow; all others very pale yellow.

E Dianisylcarbinol. 5 drops. No. 1, pinkish orange; 2 and 3, pale salmon; 4, almost invisible salmon; all others colorless.

F' Anisalcinnamalacetone. 1 drop. No. 1, carmine; 2 and 3, full red; 4, orange-red; 5, orange; 6, orange-yellow. All others clear yellow.

G' Dipiperonalacetone. 2 drops. No. 1, purplish-red; 2 and 3, full red; 4, salmon; 5, orange-yellow; 6 full yellow; all others pale yellow.

H' Dianisalacetone. 2 drops. No. 1, pinkish red; 2 and 3, full red; 4 and 5, orange-red; 6, reddish-orange; 7, brownish yellow. All others pale yellow.

I Diphenylanisylcarbinol. 5 drops. 1 to 3, brown-orange; 4 and 5, orange; 6, yellow-orange; 7, yellow; 8, pale yellow; others colorless.

J Phenylxanthidrol. 1 drop. 1 to 8, clear yellow with greenish fluorescence; 9 and 10, pale yellow; 11, colorless.

tude of the discrepancy which may be expected to arise from time to time in determining the hydrogen-ion activity by different methods in glacial acetic acid. Similar errors, often referred to as salt errors, have been found frequently in using indicators in aqueous solutions. Undoubtedly if we had varied our concentrations of base and experimented with the addition of considerable amounts of neutral salt, still larger discrepancies would have been found between the indicators and the e.m.f. measurements.

The difference in behavior of the two types of indicators in regard to the influence of the water activity was shown by several experiments. Both diphenyl- α -naphthylcarbinol (C) and piperonalacetophenone (D') show a color change at about $(P_H)^{HAc} = -2.0$. When 5 drops of acetic anhydride were added to one of two 5cc. portions of the buffer containing the carbinol indicator (C), the color rapidly became much deeper. The unsaturated ketone (D') color was unaffected. We interpret this difference as showing that the acetic anhydride combined with the small amount of water present in the solution and therefore the equilibrium with the carbinol shifted. In the case of the unsaturated ketone there was no shift as water is not involved in the reaction. In a similar experiment with diphenylanisylcarbinol in the series of 11 buffers there was no noticeable effect after several days on adding the acetic anhydride. This may

be due to the fact that the reaction between small amounts of water and acetic anhydride is slow in solutions of $(P_H)^{HAc} = -0.5$ to $+0.5$ where this indicator turns.

A few experiments in which absolute alcohol was added to the buffer solutions containing the indicators are of interest. Equal quantities (2.22 cc.) of absolute ethyl alcohol were added to 5cc. portions of buffer solution No. 4 ($(P_H)^{HAc} = -1.5$) containing, respectively, indicator F' (an unsaturated ketone) and I (a carbinol). Both solutions showed a diminution in color corresponding to a decrease in hydrogen-ion activity as would be expected from the results reported in the preceding paper. The carbinol indicator, however, showed a decrease amounting to 2 $(P_H)^{HAc}$ units (as determined by matching colors) while the change with the unsaturated ketone was only about 1 unit. Similarly 0.3 cc. of alcohol in 5 cc. of buffer No. 3 was sufficient to discharge the color of indicator C (diphenyl- α -naphthylcarbinol). With D' (an unsaturated ketone) 1.3 cc. of alcohol was necessary to produce a corresponding decrease in hydrogen-ion activity as measured by the color.

These experiments illustrate the caution which must be employed in attempting to use these indicators in solvents containing varying amounts of alcohol. Apparently alcohol can produce an alcoholysis of the carbinol salt in addition to its effect in diminishing the acidity of the solution.

In this connection it should be emphasized that the data in Table I permit of only a very rough estimation of the basicity of each carbinol or unsaturated ketone used as an indicator. As we have employed them, the turning point of the indicator is a function both of its basicity and the intensity of color of the ion. The turning point must be at such an acidity that only a fraction of the base is present as salt but what that fraction may be depends on the sensitivity of the eye for that particular color. The true measure of the basicity can only be obtained by carrying out an e.m.f. titration curve (cf. phenylxanthidrol, Fig. 1, preceding paper) or by careful colorimetric measurements in which the intensity of color is determined. Baeyer's method⁵ of determining the basicity of the halo-chromic salts by titration with alcohol suffers from this error. In his method alcohol is added until the solution is colorless; the amount of alcohol added would be a true measure of the basicity only if the sensitivity of the eye were the same for all the colored ions. It also is in error since there is not an absolute proportionality between the amount of alcohol added and the hydrogen-ion activity (cf. Fig. 4, preceding paper).

The Catalytic Effect of the Hydrogen Ion in Glacial Acetic Acid Solution

Some rough measurements were made of the rate of inversion of cane sugar in the buffer solutions listed in Table II to which a small amount

⁵ Baeyer, *Ber.*, 35, 1189, 3013 (1902).

of water was added. To 5 cc. of each buffer was added 0.1 cc. of a solution of cane sugar in water containing 7 g. in 11 cc. (7 g. of sucrose and 7 g. of water). The mixtures were kept at $25 \pm 2^\circ$ and after a given time diluted with water, neutralized with sodium carbonate and the amount of reducing sugar determined by the titration of Benedict's solution. It was assumed that the inversion was complete in 1 *M* sulfuric acid in acetic acid after five minutes; the titration of such a reaction mixture corresponded approximately to the amount of invert sugar that would be formed from the sucrose employed. Duplicate experiments agreed within 20%. Enough determinations were made in each buffer solution so that a curve representing the rate of reaction could be plotted. From this curve the time for half reaction was determined. This half reaction time is given in Table II for solutions 5 to 9 inclusive; the data were not of sufficient accuracy to warrant the calculation of a reaction constant. It is evident that the rate of inversion of the sucrose parallels in a general way with hydrogen-ion activity of the solutions. In the measurable range, $((P_H)^{HAc} = -0.8$ to $+2.2$), the rate increases 2.5 to 4.5 fold per 0.5 $(P_H)^{HAc}$ unit. If the rate were directly proportional to the hydrogen-ion activity the change would be 3.2-fold per half unit. The small amount of water added with the sucrose in each experiment made the water concentration in each experiment about 1.4 g. per 100 cc.; it is presumably this water which is involved in the inversion of the sucrose, though the acetic acid itself might take part in the reaction. The $(P_H)^{HAc}$ of the reaction mixture (Col. 3, Table II) was estimated on the basis of the experiments in the preceding paper in which water was added to various solutions (Fig. 4). Since the effect is approximately the same for all the buffer solutions except those containing sulfuric acid, the exact value for this correction is not of great importance in our preliminary work. In the range represented by solutions 4-9, the scale of hydrogen-ion activity as determined by the c.m.f. and colorimetric measurements in 99.5% acid is obviously a close measure of the rate of inversion of sucrose in the presence of small amounts of water.

TABLE II
RATE OF INVERSION OF CANE SUGAR IN 98% ACETIC ACID BUFFER SOLUTIONS

Solution	$(P_H)^{HAc}$ buffer	Est. $(P_H)^{HAc}$ of reaction mixture	Rate of inversion %	Time in minutes
1	-3.22		100	2
2	-2.7		100	2
3	-2.0	-1.8	100	2
4	-1.5	-1.3	90	2
5	-1.0	-0.8	50	2
6	-0.5	-0.3	50	7
7	0.0	+0.2	50	20
8	+0.5	+0.7	50	90
9	+2.0	+2.2	50	1400

The Behavior of Acids and Bases in Different Solvents

In themselves the results presented in this paper throw no light on the hydrogen-ion activities of acetic acid solutions compared to aqueous solutions. The excellent agreement between the electrochemical measurements and the three other methods just described only shows that each method is satisfactory for determining the relative hydrogen-ion activities in a series of acetic acid solutions. That certain acids are "stronger" in acetic acid solutions than in water rests on the electrochemical evidence presented in the last paper (with the admitted uncertainties in regard to the liquid junction) and on certain chemical facts. This chemical evidence will now be briefly reviewed.

Many very weak anhydro bases which do not form salts in aqueous solutions are neutralized by perchloric or sulfuric acids in glacial acetic acid solutions. This is shown by the titration curves which can be obtained by using the chloranil electrode or by the use of indicators. It should be noted that in the formation of salts from anhydro bases, no water is eliminated and the water activity is not involved except in so far as it affects the hydrogen-ion activity. In the second place, although perchloric, sulfuric and trichloro-acetic acids are all strong acids in water, they are of widely different strengths when dissolved in glacial acetic acid. This fact again rests not only on the electrochemical evidence but on the use of two different types of indicators.⁶ Thus whether we define the strength of acids in terms of the relative hydrogen-ion activities of their equimolal solutions or in terms of salt formation with anhydro bases, the evidence is clear that perchloric and sulfuric acids are stronger acids in acetic acid than in water. The reader of Hantzsch's papers⁷ will be familiar with the mass of evidence which he has accumulated dealing with the behavior of strong acids in non-aqueous solvents. We should like to stress Hantzsch's point that the classification of acids into strong and weak on the basis of their behavior in water is inadequate. Much important chemistry (particularly important to the organic chemist) has been obscured by our slavish devotion to water.

At present we have some information about the behavior of acids and bases in at least four common solvents, ammonia (liquid), alcohol, water and glacial acetic acid. All the facts point to a close resemblance between alcohol and water as regards the strength of acids and bases dissolved in them. We may, therefore, consider them together. Following Brönsted,⁸ we may imagine that in water the hydrogen ion (the proton) is largely hydrated. In liquid ammonia probably no one would contend that there

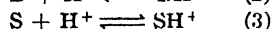
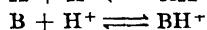
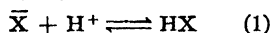
⁶ The determination of the $(P_H)^{HA}$ value of 0.2 *M* trichloro-acetic acid gave: electrometric -0.1; colorimetric +0.5 with both types of indicators.

⁷ Ref. 4 and other papers.

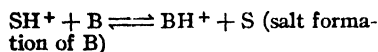
⁸ Brönsted and Guggenheim, *THIS JOURNAL*, 49, 2554 (1927).

was any large proportion of free hydrogen ion in equilibrium with the solvated hydrogen ion which is the ammonium ion. We are thus led to imagine that the essential difference between glacial acetic acid and water is similar to that between water and liquid ammonia. The acetic acid molecule has less affinity for a proton than water; the ion $\text{CH}_3\text{COOH}_2^+$ more readily gives up its extra proton than the ion H_2OH^+ .

The formation of a salt from an anhydro base is the reverse of the dissociation of an acid. Indeed, if we accept Brönsted's definition of a base, the anhydro base (B), the anion of an acid ($\bar{\text{X}}$) and the solvent molecule (S) may all be regarded as bases competing for the proton (H^+). We may, therefore, write the following equations



Probably in most solvents the amount of unhydrated hydrogen ion (free proton) is very small⁸ but this does not prevent our formulating the reaction



in terms of the competing reactions 2 and 3 above. A very weak base, B, (corresponding to a very strong acid BH^+) will only form stable salts in a solvent which has considerably less affinity for the proton than B itself. Obviously salt formation can only take place with an acid whose anion ($\bar{\text{X}}$) will release the proton to B.

The inter-relation of the three competing reactions can best be illustrated qualitatively by a diagram. This is shown in Fig. 1; the affinities of the three competing bases ($\bar{\text{X}}$, S and B) are plotted vertically on lines 1, 2 and 3, respectively. The position of some common acids, anhydro bases and three solvents are indicated by their formulas. The scale is arbitrary and no attempt has been made to evaluate the exact relation-

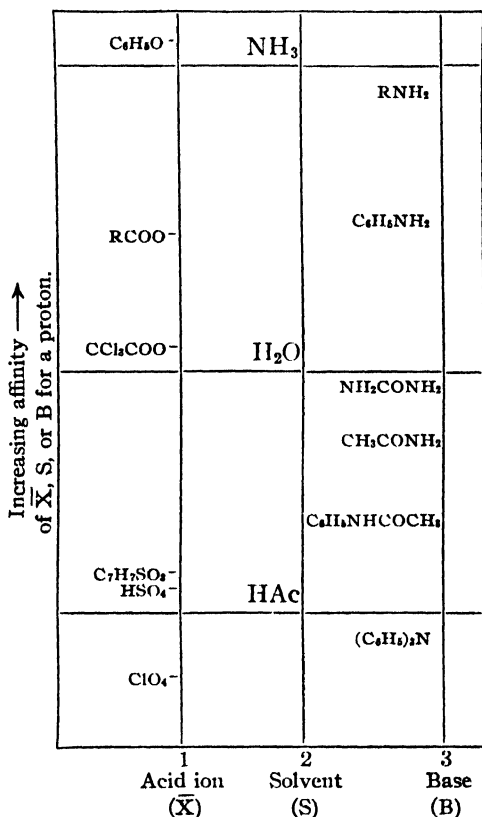


Fig. 1.—Diagram illustrating the relationship of acids and anhydro bases in a variety of solvents.

ships as this would involve data in regard to the activities which are lacking. According to the general scheme which is roughly outlined in Fig. 1, acids are "strong" only in the solvents which lie above them on the diagram. Thus perchloric acid is strong in all three solvents; sulfuric and hydrochloric acids in ammonia and water and RCOOH only in ammonia. Anhydro bases are neutralized by one equivalent of any acid which is a stronger acid than their "onium ions," provided the action takes place in a solvent which lies below the position of their ions on the scale. Thus an amide (RCONH_2) will be neutralized only in acetic acid and only by perchloric or sulfuric acid. We have not yet found a solvent in which triphenylamine can be titrated even with perchloric acid. If such a solvent is found it will lie below acetic acid in the diagram.

We take pleasure in expressing our indebtedness to Mr. N. M. Bigelow for assistance in carrying out the experiments on the inversion of sucrose.

Summary

1. Five arylcarbinols and five unsaturated ketones have been tested for the appearance of halochromic color by introducing them into eleven buffer solutions in glacial acetic acid. The results are all consistent with the determination of the hydrogen-ion activities of the solution by means of the chloranil electrode. The ten substances form a graded series of indicators suitable for use in superacid solutions.

2. The rate of inversion of sucrose in 98% acetic acid solutions of definite acidity has been studied. The rate is approximately proportional to the hydrogen-ion activity as measured by the chloranil electrode or by the use of indicators.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]
**APPLICATION OF THE INTERFERENCE REFRACTOMETER TO
THE MEASUREMENT OF THE CONCENTRATION OF DILUTE
SOLUTIONS¹**

BY RUDOLPH MACY

RECEIVED AUGUST 19, 1927

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In this Laboratory an extended series of measurements has been made involving accurate determinations of the concentrations in water of various types of organic compounds. A more accurate, more general and more rapid method of determining concentrations in liquid solvents was sought than is afforded by the usual methods of analysis. The instrument selected for this purpose is the interference refractometer designed by Professor F. Haber and made by the Zeiss Company. Although measurements can be made very quickly by means of this instrument, and with a high degree

¹ Published by permission of Chief, Chemical Warfare Service.

of accuracy, it is also found to be very misleading if some of the precautions to be explained in this paper are not observed. Since it is likely that this type of interferometer is being used by other investigators for analogous purposes, it was thought advisable to publish this account of some anomalies in its behavior. It is hoped that the interpretation given here will be of value to other users. The writer is not aware of any published articles referring to the nature of the calibration lines which are essential in the routine analyses made with the interferometer.²

The Instrument

The principle employed in the Zeiss type of interferometer was developed originally by Rayleigh in order to measure the refractive indices of the rare gases. A discussion of the fundamental principle involved can be found in the textbooks by Travers,³ and by Reilly.⁴ Pamphlets describing the instrument can be obtained from the manufacturer,⁵ these contain a complete bibliography which includes references to the original articles by Rayleigh and Haber.

The instrument used in the work reported in this article is the portable type in which an easily accessible cell is employed to hold liquids. The interferometer cell consists of two parallel compartments separated by a narrow partition, with plane lenses cemented at each end. It rests in a bath of water at constant temperature. By means of a system of prisms and mirrors two vertical beams of white light from a 4-volt lamp are passed through the cell. Each beam passes *through* one compartment of the cell and also *underneath* the cell through the water in the bath. The two lower halves of the beams interfere and give rise to a series of interference bands which are represented by the lower set in Fig. 1. The interference of the two upper halves of the beams which traverse the cell yields the upper series of bands. These spectra are observed through a microscope arrangement.

When both compartments of the interferometer cell are filled with water the upper interference spectrum is identical with the lower. There are three distinct transverse bands, the middle one being dense black, with practically no color fringes. The bands to the right and left of the central black reference line, however, are fringed with colors as shown in the accompanying illustration. If now the water in the left compartment

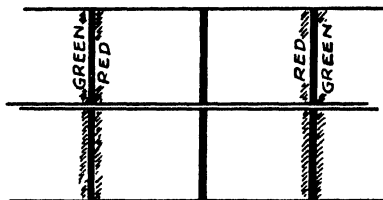


Fig. 1.—Appearance of the colored fringe systems when upper movable spectrum and lower fixed spectrum are matched.

² Since the time this article was written and submitted for approval to the military authorities a recent paper by W. Barth, *Z. wiss. Phot.*, 24, 145 (1926), has come to the author's attention through *C. A.*, 21, 1749 (1927). The paper by Barth includes a large number of references which are not cited by Carl Zeiss and which discuss the same phenomena presented in this article. On some important points there are discrepancies between the experimental observations by Barth and by myself.

³ Travers, "Study of Gases," Macmillan and Co., New York City, 1901.

⁴ Reilly, "Physico-Chemical Methods," D. Van Nostrand Co., New York City, 1926, p. 521.

⁵ "Industrial Interferometers," and "Interferometers for Gases and Water," Carl Zeiss, New York.

be removed and replaced by a very dilute solution the upper system of bands will be displaced to the left. By means of a compensating lens, operated by a graduated micrometer screw which reads from 0 to 3000 units, the bands are brought back into the field of vision and the spectra are matched up once more. By varying the concentration of the solution and noting the micrometer reading after the bands are matched, a straight calibration line can be constructed as indicated in Fig. 2 by the segment OC of the curve OD.

From this calibration line the concentration of an unknown solution can be read off when its interferometer reading has been determined. Instead of plotting a line as in Fig. 2 it is convenient simply to find the slope of the line, thus

$$\text{factor, or value of 1 scale unit} = \frac{y \text{ mg. per liter}}{x \text{ units}}$$

The slope of the line, or factor, can be found by reading one solution of known concentration, which involves just one or two weighings. The concentration of any solution of the same substance can then be determined simply by multiplying this factor into its interferometer reading.

Observations on the Instrument

I. Additive Properties.—A number of determinations have shown that the interferometer reading for two substances in the same solution is very nearly, although not exactly, the sum of the readings of each taken separately. This phenomenon had an important bearing on some of the work done in this Laboratory.

II. Relation between Sensitivity of the Instrument and Molecular Structure.—A number of organic compounds have been studied in the course of other work and several generalizations can be drawn from the data already at hand. In the following table, instead of expressing the concentrations in milligrams per liter, they are given in millimoles per liter in order to present figures which

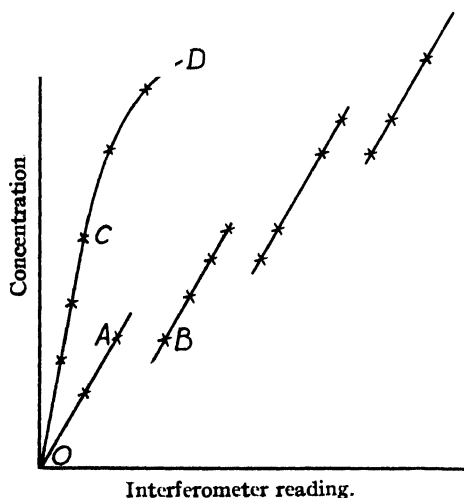


Fig. 2.—Typical calibration curves (schematic).

are theoretically more comparable. These figures indicate that for the simpler aliphatic and aromatic compounds it requires a smaller concentration of an aromatic compound to change the scale reading one unit or, in general, the interferometer is more sensitive to aromatic compounds. For both types of compounds there is a general increase in sensitivity with increase in molecular complexity.

TABLE I
FACTOR, OR VALUE OF 1 SCALE UNIT IN MILLIMOLES PER LITER
(Length of cell = 4 cm.)

Aliphatic compounds		Aromatic compounds	
Acetone	0.115	Phenol	0.025
Urethan	.059	Phenylurethan	.018
Chloro-acetone	.058	Chloro-acetophenone	.018
Sulfonal	.019	Piperonal	.017
Sucrose	.011	Coumarin	.00685

III. Anomalies in the Calibration Lines.—When a solution is placed in one compartment of the interferometer cell, with pure water in the other, and the spectra are matched up by turning the micrometer screw, it is found that the central black band of the upper spectrum is usually no longer pure black but is tinged with green. However, even though this reference band suffers a slight change in its appearance it is easily followed and is readily matched. This is proved by the fact that the calibration line of such a compound as urethan is a straight line up to the appreciably high concentration of 3 g. per liter. (See the straight segment OC of the curve OD in Fig. 2.)

When urethan is studied at higher concentrations than 3 g. per liter it is found that the calibration line OD deviates slightly from a straight line function and becomes a smooth continuous curve which has been followed up to a concentration of 10 g. per liter. The phenomenon of curvature has been proved for a large number of compounds which have comparatively high solubilities in water. The deviation from a straight line at high concentrations may be due to a closer packing of the solute molecules and may therefore be considered simply another abnormal behavior of concentrated solutions.

A large number of compounds have been studied whose solubilities in water are less than 1 g. per liter. In these cases, moreover, since it was necessary to determine concentrations to at least 5 mg. per liter, the calibration curves had to be constructed with great care. Most of these slightly soluble compounds were benzene derivatives, and all these aromatic compounds yielded calibration curves illustrated in Fig. 2 by the series of broken lines beginning with OA. These lines for any one compound are all of the same slope and overlap slightly; and the horizontal distance between two adjacent lines is 13 interferometer scale units for all compounds.

The writer's interpretation of this phenomenon of the stepwise breaks in the calibration line is as follows. It has been stated that when a solution is placed in the cell the central black band of the upper interference spectrum becomes tinged with green. In the case of most compounds this green fringe grows wider as the concentration increases; as this reference band grows wider the next band to the left of it grows narrower and the red

fringe originally on it becomes less distinct. In a certain range of concentrations it is difficult to distinguish between these two bands since they have practically no red coloration. In such a case it is best to record the readings of both lines; expressed graphically in Fig. 2 the scale readings would be 13 units apart as represented by points A and B. The calibration lines are removed from one another by 13 units on the horizontal axis because of the fact that the distance between two adjacent bands in the interference spectrum is equivalent to that number of divisions on the micrometer screw.⁶

At concentrations slightly higher than that represented by points A and B, the lines become more easily differentiated again and it is a simple matter to match up the two interference spectra. However, the black line which

TABLE II
CALIBRATION DATA
(Length of cell = 4 cm.)

Urethan		Sodium nitrate		Potassium dichromate (continued)	
Mg./liter	Reading	Mg./liter	Reading	Mg./liter	Reading
0	0	0	0	300	134
121	23	94.8	21	335	145
242	45	189.6	41	400	166
363	66	284.4	61	447	182
484	87	379.2	81		
605	112	474	101	447	195
1214	233			500	211
2000	375	474	114	558	231
3000	565	663.6	153	600	245
7000	1359	758.4	174	600	258
10000	1994	948	214	625	267
Phenylurethan		Potassium dichromate		670	281
0	0	0	0	700	290
94	31	25	8	700	303
187	63	25	21	782	318
		50	28		
187	76	100	45	782	331
281	107			800	336
375	138	100	58	800	349
		150	75	900	382
375	151	200	90		
469	185	250	105	900	395
562	216	300	121	1000	428
562	229				
656	260				
750	293				
844	327				

⁶ According to Barth (ref. 2) the distance between spectral lines varies along the scale, in his instrument the variation being from about 18 to 28 scale units. On this basis Barth builds up an equation by means of which a standard calibration line can be calculated.

is now being used as a reference originally held a red fringe. The process by which the central black band gains a red fringe and the adjacent band to the left loses its red fringe continues with marked regularity for most aromatic compounds. For example, phenylurethan solutions show the phenomenon at every increase in concentration of 180 to 200 mg. per liter. The data in Table II are grouped according to the number of broken lines; when plotted on millimeter cross section paper the lines appear as illustrated in Fig. 2. Dilutions were all made by means of calibrated burets

That the change in coloration of these spectral lines is due to the difference in dispersion of white light by the solution and by pure solvent has already been noted quite often in the literature⁷ In Table II are given the data for the calibration of the yellow solution of potassium dichromate which was studied in order to observe the effect of color on the calibration lines. Even at the low concentration of 25 mg. per liter in a 4cm. cell this causes a shift of one wave length in the spectrum. The complete calibration of the compound resulted in a stepwise shift of eight bands up to a concentration of one gram per liter, but the phenomenon did not occur at periodical increases in concentration as found for colorless solutions. In the same range of concentrations the colorless solution of sodium nitrate causes only one shift in the black reference line and this occurs just above the concentration of 500 mg. per liter.

It is evident, therefore, that a complete calibration curve over the entire range to be studied is essential in the case of most compounds. The aliphatic compounds do not, as a rule, bring about a break in the calibration curve below one gram per liter. Even a more complex substance such as sucrose has been found to give a straight, unbroken line. In regard to the curvature of the calibration lines of aliphatic compounds at higher concentrations, which has already been noted, it may be stated that there has been no explanation in the literature and none will be offered here.

The abnormal effect of the benzene ring on white light is shown by the results obtained with thymol and menthol. These are very much alike, but differ in that thymol contains the benzene ring in the unreduced state. Over a range of 500 mg. per liter thymol causes a shift of 2 bands in the spectrum, while menthol causes none.

It may be noted that Mitchell⁸ reported the use of a Jamin⁹ type of interferometer for solubility measurements. This instrument employs monochromatic light and the calibration lines obtained with it by Mitchell are all continuous. The technique in the use of the Jamin instrument is not so simple as for the Zeiss type in that the interference bands of mono-

⁷ Barth and his references (ref. 2) ascribe the breaks in the calibration lines to differences in the refraction between glass lenses, solution and distilled water.

⁸ Mitchell, *J. Chem. Soc.*, 129, 1333 (1926).

⁹ Jamin, *Ann. chim. phys.*, 52, 171 (1858).

chromatic light are all alike and the displacement must be carefully followed on the cross hairs of a telescope.

IV. Length of Cell.—The maker of the instrument supplies cells varying in length from 0.1 cm. to 8 cm. The observation has been confirmed that the micrometer reading, that is, the displacement of the bands, is proportional to the length of the cell. The longer cell, therefore, increases the accuracy of the measurements.

In the case of benzene derivatives the longer cell increases the optical effects which have just been described. For example, using a 4cm. cell the breaks in the calibration of thymol occurred regularly with each increase in concentration of about 200 mg. per liter. When using an 8cm. cell this phenomenon occurred at about every 100 mg. per liter.

The writer wishes to express his thanks to Dr. A. L. Kibler, Chief of the Physical Chemistry Department for his advice, and to Mr. G. A. Sachs for his assistance in the laboratory.

Summary

Some observations are reported on the use of the Zeiss interference refractometer as a means of determining the concentrations of dilute solutions

EDGEWOOD, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

SELENO COMPOUNDS OF TUNGSTEN¹

BY VICTOR LENHER AND AUGUST G. FRUEHAN

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Since selenium is similar to sulfur in many respects, it was believed to be possible to prepare some new compounds of selenium which would be analogous to known compounds of sulfur. Thus, seleno-antimonates, seleno-arsenates and seleno-stannates are known which are analogous to the thio-antimonates, thio-arsenates and thio-stannates. Many mixed compounds such as $\text{Na}_3\text{SbSeS}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Na}_3\text{AsSe}_2\text{S}_2 \cdot 9\text{H}_2\text{O}$ have also been prepared. Thio-compounds of tungsten, molybdenum and vanadium such as $(\text{NH}_4)_2\text{WS}_4$, $(\text{NH}_4)_2\text{WO}_2\text{S}_2$, $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{NH}_4)_3\text{VS}_4$ are known, but analogous seleno compounds have not been reported. It is the purpose of this investigation to attempt the preparation of seleno compounds which are analogous to the thio-tungstates.

Uelsmann² prepared tungsten triselenide by saturating a tungstate with hydrogen selenide and then acidifying the solution with sulfuric acid, when the tungsten triselenide was precipitated. It was logical to

¹ From part of a thesis to be submitted by August Fruehan in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

² Uelsmann, *Jahresbericht*, 1860, 92.

believe that the solution which he had saturated with hydrogen selenide contained a seleno-tungstate and efforts were directed to crystallize a seleno-tungstate from a concentrated solution of ammonium tungstate which had been saturated with hydrogen selenide.

Preparation of Materials

Elementary Selenium.—A rapid stream of sulfur dioxide was passed into a hot hydrochloric acid solution of selenium dioxide. The selenium was filtered, washed with hot water, then with alcohol and finally with ether. It was dried at 105°.

Hydrogen Selenide.—The method of Moser and Doctor³ was used to prepare the hydrogen selenide.

Tungstic Oxide.—Tungstic oxide, WO_3 , was prepared from well-crystallized sodium tungstate. Sodium tungstate was treated with hydrochloric acid and evaporated to dryness. The sodium chloride was dissolved out of the dried mass with hot water and the tungstic oxide was filtered, washed and dried. An analysis of the sodium tungstate showed good agreement with the formula $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

Preparation of Seleno-tungstates

Procedure

A solution of ammonium tungstate was prepared by adding an excess of tungstic oxide to ammonium hydroxide of specific gravity 0.90 and filtering off the excess of the oxide. The ammonium tungstate solution was placed in a reaction chamber which consisted of a 250cc. wash bottle with an enlarged delivery tube to prevent stoppering of the tube with the crystalline product. Nitrogen was used to sweep the air out of the system. Hydrogen selenide was then passed through the ammonium tungstate solution. During the course of the reaction heat was liberated, the solution changed to a dark brown color and crystals deposited on the sides of the container. Cooling of the reaction chamber caused more crystals to deposit from solution. During some of the early experiments it was noted that sometimes dark green crystals would be formed and at other times red ones would be obtained.

The green crystals were found to be ammonium seleno-tungstate $(\text{NH}_4)_2\text{WSe}_4$, as will be shown later, and the red ones ammonium diseleno-tungstate $(\text{NH}_4)_2\text{WSe}_2\text{O}_2$. When the ammonium tungstate solution was saturated with hydrogen selenide, the green crystals were obtained, and the red crystals deposited from the solution when it was incompletely saturated with hydrogen selenide.

From the knowledge of the ease of oxidation of other seleno compounds it was anticipated that the preparation, filtration and washing of the crystals would necessitate the process being carried out in the absence of oxygen. Both crystalline compounds were treated in the same manner after removal from the chamber.

The crystals, together with enough of the mother liquor to cover them, were transferred to the filter as rapidly as possible to avoid oxidation. The small amount of oxidation which occurred during the transfer was confined to the mother liquor. The crystals were washed first with alcohol, then with ether to displace the alcohol and finally with carbon disulfide to dissolve traces of selenium which might cling to the crystals from the mother liquor. The carbon disulfide was purified by shaking it with phosphorus pentoxide and mercury and then distilling it. The crystals were finally dried for several hours in a current of hydrogen. Oxygen was removed from the hydrogen by passing the gas over hot copper gauze and moisture was removed by passing the gas through sulfuric acid and phosphorus pentoxide.

³ Moser and Doctor, *Z. anorg. Chem.*, **118**, 284-292 (1921).

Methods of Analysis

Determination of Ammonia.—Ammonia was determined by adding an excess of sodium hydroxide and distilling the liberated ammonia. Tenth normal acid was used to collect the ammonia and the excess acid was titrated with tenth normal alkali, using methyl orange as an indicator.

Determination of Tungsten.—Tungsten was determined by igniting the sample in a porcelain crucible over a Bunsen burner. The tungstic oxide, WO_3 , which remained after the ignition was weighed.

Determination of Hydrogen.—Although the analysis of the red crystals showed good agreement with the formula $(NH_4)_2WSe_2O_2$, it was thought advisable to determine the hydrogen. Such a determination would necessarily reveal the presence of water. Combustion of the compound was carried out in the ordinary manner with the exception that a plug of potassium chromate was placed in the combustion tube to retain selenium dioxide.⁴ The sample in the boat was also covered with potassium chromate.

Determination of Selenium.—The determination of selenium required an oxidation of the compounds, a separation of the tungsten from the selenium and a precipitation of selenium as the element. Oxidation was carried out in a Parr sulfur bomb. The charge was made up in the following manner. Approximately 14.0 g. of sodium peroxide was mixed with 0.60 g. of starch and the mixture divided into two equal parts. The sample was mixed in the bomb with one of these parts and the second part placed on top of the mixture containing the sample. The fuse wire was arranged so that it was suspended in the upper mixture. After firing the charge, the material in the bomb was dissolved out with water and the solution boiled for a few minutes to decompose the hydrogen peroxide. The solution was then cooled and strongly acidified with hydrochloric acid. Tungstic acid was precipitated in the acid solution. Precipitation and coagulation were completed by adding a few cubic centimeters of a hydrochloric acid solution of cinchonine. The precipitate was filtered on a Gooch crucible and washed with a cinchonine solution. Repeated tests for selenium in the precipitate containing the tungsten showed that a good separation of tungsten from selenium was obtained with a single precipitation.

To one volume of the filtrate containing the selenium in the form of selenic acid were added one volume of hydrochloric acid (sp. gr. 1.20) and one volume of the same acid which had been saturated with sulfur dioxide. The solution was allowed to stand until most of the selenium had settled to the bottom of the beaker. The supernatant liquid was poured through a Gooch crucible and the sodium chloride which had precipitated with the selenium from the strong hydrochloric acid solution was dissolved with water. Before transferring the selenium to the Gooch crucible it was washed with strong hydrochloric acid and then changed to

⁴ Julien, *THIS JOURNAL*, **47**, 1799 (1925).

the black variety by treatment with hot water. The selenium was washed first with hot water, then with alcohol and finally with ether. It was dried at 105° and weighed.

Results

The results of the analysis are given in the following tables.

TABLE I
AMMONIUM SELENO-TUNGSTATE, $(\text{NH}_4)_2\text{WSe}_4$

	Found, %			Calcd., % $(\text{NH}_4)_2\text{WSe}_4$
	1	2	3	
W	34.22	34.04	34.38	34.27
NH_4	6.34	6.44	6.50	6.33
Se	59.45	58.85	58.90	59.01

TABLE II
AMMONIUM DISELENO TUNGSTATE, $(\text{NH}_4)_2\text{WSe}_2\text{O}_2$

	Found, %			Calcd., % $(\text{NH}_4)_2\text{WSe}_2\text{O}_2$
	1	2	3	
W	44.92	44.91	44.73	44.83
NH_4	8.40	8.38	8.45	8.30
Se	38.30	38.45	38.60	38.50
H_2	1.97	1.99	...	1.96

The experimental values are seen to be in close agreement with the calculated ones. The results for the hydrogen show that the compound contains no water of crystallization.

Properties of Seleno-tungstates

Crystals of ammonium seleno-tungstate and ammonium diseleno-tungstate which have been carefully washed and dried do not show any discoloration when kept in a calcium chloride desiccator for several months. However, a slight odor which resembles hydrogen selenide can be detected.

Both the seleno-tungstate and the diseleno-tungstate are readily soluble in water, somewhat soluble in alcohol, but insoluble in ether, benzene and carbon disulfide. The seleno-tungstate yields a red aqueous solution which is slowly decomposed in the air, giving a brown precipitate. The precipitate is probably a mixture of selenium and tungsten triselenide, WSe_3 . The diseleno-tungstate gives an aqueous solution which is similar in color to a solution of potassium dichromate but the color of concentrated solutions is also red. Aqueous solutions of the diseleno-tungstate are slowly decomposed in the air and a precipitate of red selenium is formed.

Green crystals of ammonium seleno-tungstate are reddish-brown in a finely pulverized state. In order to minimize oxidation, the crystals were pulverized under benzene.

Through the kindness of Professor A. N. Winchell of the Department of Geology of the University of Wisconsin we are publishing the following optical study which he has made of these new compounds.

Crystals of ammonium seleno-tungstate are yellowish-green in color with bright metallic luster; they gradually tarnish to a dark purple. The streak is reddish-brown which alters to black in a few days' time. The crystals are not entirely opaque under the microscope, although they are very dark and are opaque except with maximum illumination, high power and very thin flakes, which transmit a deep red color. The crystals seem to be rectangular parallelepipeds; they are not isotropic and are, therefore, not isometric; a thin flake probably parallel with a cleavage seems to be normal to a bisectrix, but the mineral is so dark-colored that greater precision is not possible. If these properties are correctly determined, the crystals are biaxial and orthorhombic and are bounded by 001, 010 and 100. They are probably isomorphous with the analogous sulfur compound $(\text{NH}_4)_2\text{WS}_4$.

The indices of refraction seem to be higher than 1.74.

Crystals of ammonium diseleno-tungstate have a brownish-red color and an adamantine luster; they are complex with numerous small faces, but have a short prismatic habit. Under the microscope a fragment nearly normal to an optic axis shows very little curvature of the isogyre; consequently the optic angle ($2V$) is nearly 90° ; the optic sign is positive. The birefringence is extreme and the dispersion is very strong; in both of these characters the mineral resembles titanite, though quantitative measures have not been made. One optic axis is nearly normal to a cleavage, which may be taken for a basal cleavage, since one such fragment shows four very low pyramid faces, nearly symmetrical; in this case the optic axis is out of center about one-third the radius of the field and roughly in the 100 plane. The angle between the prism faces (110 to $1\bar{1}0$) measured in this fragment and therefore presumably in the 001 plane is 109° . The dispersion seems to be unsymmetrical, and extinction in white light is incomplete in some cases because the dispersion is so strong.

In thin plates, probably about .03 mm. in thickness, the pleochroic colors are as follows: X = light (yellowish) green; Y = greenish-yellow; Z = brownish-yellow. All the indices of refraction are above 1.74.

Assuming a thickness of .03 mm. in one plate, the interference colors indicate that $N_m - N_p = 0.045$.

All these properties make it probable that these crystals are triclinic and isomorphous with crystals of $(\text{NH}_4)_2\text{WS}_2\text{O}_2$.

Summary

Ammonium seleno-tungstate, $(\text{NH}_4)_2\text{WSe}_4$, and ammonium diseleno-tungstate, $(\text{NH}_4)_2\text{WSe}_2\text{O}_2$, have been prepared and analyzed. Some of their properties, including the crystal form, have been studied.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

**SELF-INTEGRATING CHEMICAL ACTINOMETRY FOR
ULTRAVIOLET DOSAGE OR OTHER SPECIFIC PURPOSES**

BY MERRILL JAMES DORCAS AND GEORGE SHANNON FORBES

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A good chemical actinometer must accurately predict the photochemical reaction rate, x , in a second system as a definite function of, y , its own rate when exposed to the same light source. The implied condition is, of course, that absorption is complete and $x_{\lambda_1}/y_{\lambda_1} = x_{\lambda_2}/y_{\lambda_2} = x_{\lambda_3}/y_{\lambda_3}$ for all wave lengths involved. While all this has long been realized, actinometers in general have relied upon guess work or lucky compensations of effects to attain the desired end.

The Ives physical photometer^{1,2} automatically integrates, at any instant, in terms of thermopile deflection, the luminous equivalent of a polychromatic light source as seen by the average human eye. A filter, between source and thermopile, transmits for each wave length a fraction of incident radiation proportional to its luminous efficiency. Thus the total relative "brightness" of two sources differing widely in spectral energy distribution can properly be compared. The magnitude of any other photochemical effect could be similarly referred to the response of any non-selective radiometer if the sensitivity curve for the effect were given.

Radiometry by thermopile or bolometer requires cumbersome apparatus, favorable environment and considerable experience. A device for integrating, by chemical means, the total efficiency, for a given photochemical purpose, of any polychromatic light source ought to be widely useful. Because of the present interest in ultraviolet dosage we submit the following, with emphasis upon the general applicability of the method. Eidenow³ has discussed (with bibliography) six different devices, physical or chemical, for predicting relative efficiencies of various light sources in producing erythema (sunburn) on human skin. These include liberation of iodine from hydriodic acid, silver halide papers, selenium cell, Keller's modified iodide solution, time required to kill infusoria and Webster's methylene blue acetone. Other devices are the darkening of lithopone,^{4,5} the uranyl oxalate actinometer,⁶ cadmium photoelectric cell,⁷ and total energy transmitted by a silver film.⁸ Of these methylene blue, the cad-

¹ Ives, *Trans. Illum. Eng. Soc. N. Y.*, **10**, 101 (1915).

² Coblenz and Emerson, *Bur. Standards Bull.*, **14**, 231 (1918).

³ Eidenow, *Lancet*, **209**, number 5320 (1925).

⁴ Pfund, *Proc. Am. Soc. Testing Materials*, **23**, II, 369 (1923).

⁵ Janet Clark, *Am. J. Physiol.*, **69** (1924).

⁶ Moss and Knapp, *J. Soc. Chem. Ind.*, **44**, 453 (1925).

⁷ Griffith and Taylor, *J. Hyg.*, **44**, 453 (1925).

⁸ Miethe and Stenger, *Z. wiss. Phot.*, **19**, 57 (1919).

mium cell and the silver film have sensitivity curves very roughly corresponding to that of the erythema reaction. But evidence is lacking that any of the above give reliable predictions when used with light sources of widely differing spectral energy distributions, and theory predicts that they could not do so, especially as they respond to light of wave lengths outside of the range productive of erythema.

Hausser and Vahle⁹ isolated seven monochromatic radiations, measured intensities by thermopile and times required to produce a standard erythema. Their plot of efficiency against wave length is unsymmetrical and extends from 313 $m\mu$ to 254 $m\mu$ and beyond with a peak at 297 $m\mu$.

We selected for the actinometer reaction the photolysis of *p*-benzoquinone in fifty per cent. alcohol. Dr. P. A. Leighton, instructor in chemistry in this Laboratory, has investigated this reaction, proving the quantum yield practically constant between 313 $m\mu$ and 254 $m\mu$. Analysis by iodimetry proved a further advantage. We are very grateful to Dr. Leighton for permission to use these and other facts in advance of the publication of his own paper.

As the curve of Hausser and Vahle is based on ergs, not quanta, we multiplied its ordinates by numbers inversely proportional to the corresponding wave lengths, and replotted. The ordinates thus corrected gave directly the proper relative transmissions of the ideal filter, since the amount of light transmitted at any wave length must photolyze a mass of quinone proportional to the erythema-producing power of the corresponding light component in the original source. The assumption that all the monochromatic effects can be integrated by summation appears reasonable in this case, as no induction period exists and only a few per cent. of the reaction mixture is decomposed. The rate of photolysis of quinone behind the filter is then proportional to the physiological effect of the naked source if the reciprocity law holds for both reactions.

Examination of data on light transmission suggested that the following, plus a suitable absorbent for the visible spectrum, might meet our requirements: quinine, α - and β -naphthylamine, triphenylmethane, auramine, Sudan G, tartrazine, α - and β -naphthol, stypticine (cotarnine) and carbostyryl. Using a spectro-radiometer kindly loaned by Dr. P. A. Leighton, we measured their transmissions and found that none would do even when the solvent was varied. Later we discovered a promising spectrogram of picric acid by Uhler and Wood¹⁰ and developed a filter having 1 cm. of 0.00025 *M* picric acid between a sheet of red-purple Corex glass 2.5 mm. thick and one of clear Corex. Fig. 1 superposes the transmission curve, B, of this combination upon the ideal transmission curve described above, A. The transmissions on the left are too great, but roughly com-

⁹ Hausser and Vahle, "Strahlentherapie," 13 (1923).

¹⁰ Uhler and Wood, *Carnegie Instit. Wash. Pub.*, 1907.

pensate for the complete extinction of the relatively inefficient region beyond 270 $m\mu$. We know of no practical light source whose emission in the last-mentioned region is large in comparison with that between 313 $m\mu$ and 270 $m\mu$. Red light, which is transmitted by this filter, has no effect on quinone. While this filter is not perfect, it sufficed for present purposes. The picric acid solution was changed after each experiment in spite of the fact that its transmission was not greatly altered by the exposure. To the back of the clear Corex plate was cemented a second glass ring, 5 cm. in diameter and 3 cm. long, also having a tubulure. To the rear edge of this ring was cemented a plate of ordinary glass completing a cell of 45cc. capacity.

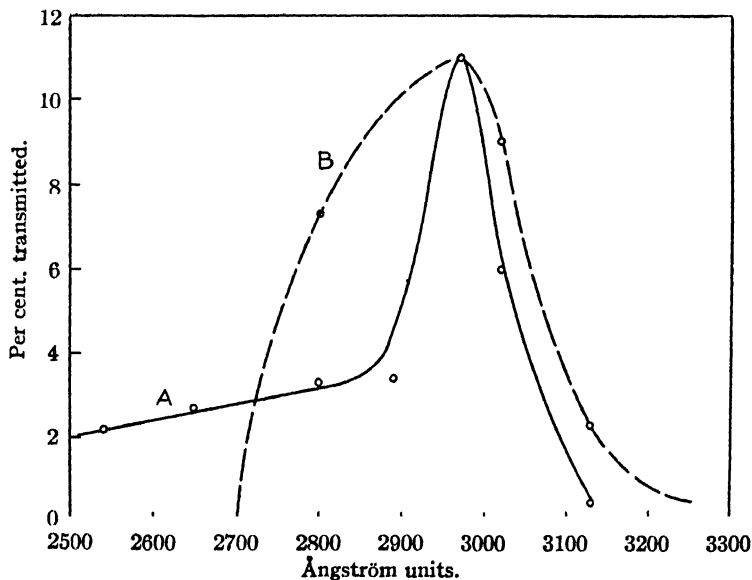


Fig. 1.

Quinone, three times sublimed at the lowest possible temperature, was dissolved in 50% ethyl alcohol to form 100 cc. of 0.002 M solution. The alcohol had been fractionated, preserving only the middle portions. This solution must be made up just before use, as its absorption spectrum varies somewhat with time. It absorbs the "erythema light" completely.

Figure 2 shows the arrangement of apparatus, unchanged during the measurements. The light source was an arc between 5 mm. carbon rods, cored or uncored,¹¹ set up in a feeding mechanism regulated constantly by hand, maintaining always an alternating current of 10 amperes with an

¹¹ Spectral energy distribution curves by Coblentz, Dorcas and Hughes, *Bur. Standards Sci. Paper*, 539, 548 (1926).

arc voltage of 50. To accelerate the photolysis we used two quartz condensers each 11 cm. in diameter and 17 cm. in focal length, such as are found in moving picture projectors. Next came a quartz cell 50 mm. square and 2 cm. thick, filled with circulating water to cut down the infrared. We believe that the spectral energy distribution of the source was not affected seriously, for our purposes, through absorption and reflection by condensers and water cell. The filter and reaction cell followed, kept cool by an air blast. The diverging cone of long ultraviolet just filled the cell.

Forty-five cc. of quinone was delivered into the cell by a special pipet and the same volume into a dark vessel beside it. After irradiating the

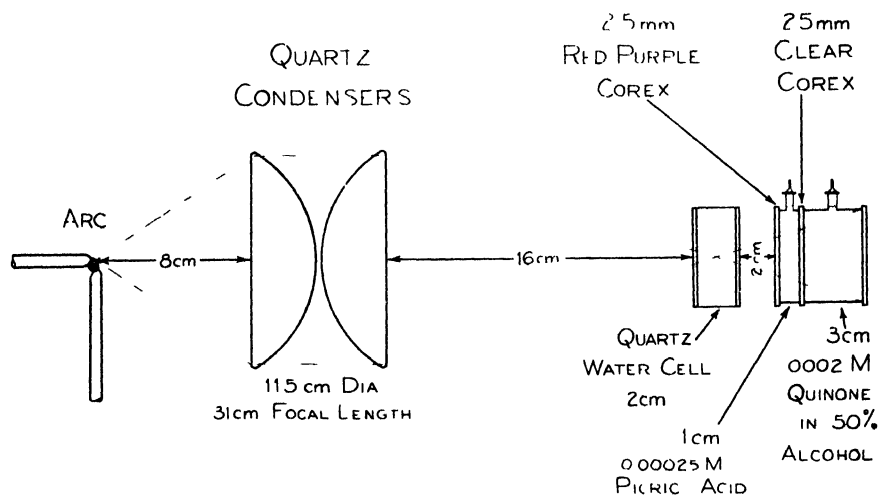


Fig. 2.

first for about two hours, both were cooled in ice and titrated simultaneously with 0.004 *N* thiosulfate, adding 10 cc. of 1 *N* iodide and of 1.5 *N* hydrochloric acid at the start, with starch at the end. The difference was taken as a measure of photolyzed quinone, with elimination of the small dark reaction, and of oxidation by air during titration.

The results appear in Fig. 3. Quinone photolyzed per hours, y , is plotted vertically against x , the reciprocal of the time necessary to produce a uniform erythema upon the skin of one of us, using the same carbons with 20 amperes instead of 10, a variation not likely to upset *relative* efficiencies. The point *K* was closely checked by a duplicate experiment; as the spectral energy distribution of the cobalt arc¹⁰ is not extraordinary its small divergence can safely be attributed to uncertainties in comparing skin colorations. Roughly, $y = ax$. For the more efficient sources, a line of the type $y = ax + b$, where b is relatively small, is a better approximation. The change in slope is not due to absorption by reaction products

but this might make trouble if quinone photolysis exceeded 15% of the whole. We hope to follow up the indication of a threshold intensity. Apparently the reciprocity law does not hold exactly for the erythema reaction and here our results are at variance with those of Hausser and Vahle. We believe that the actinometer described above is more sound in principle and reliable in performance than others proposed for the purpose in question. It will integrate variations in total intensity and in spectral energy distribution over the period of its use. Such actinometers could not be recommended for general photochemical research, because

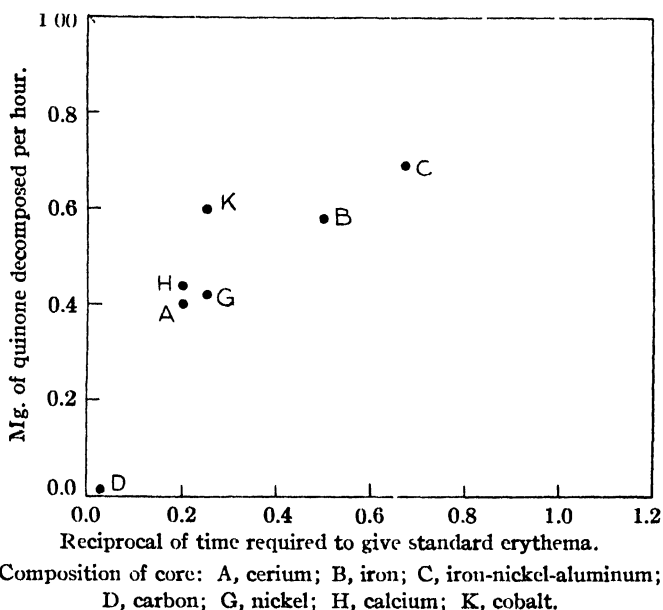


Fig. 3.

the radiometric work with monochromatic light needful to establish the two sensitivity curves and the proper filter would better be applied directly to the solution of the problem in hand. They should be useful, however, to study any single photochemical effect where many experiments must be made in various places. Among these are photography, where sensitivity curves are known; antirachitic therapy, whose curve should soon be available, and even chlorophyll assimilation, whose curve or curves, when known, might prove hard to reproduce in a filter.

Summary

Red-purple Correx glass, plus 1 cm. of 0.00025 *M* picric acid, transmits, at each frequency, light wattage proportional to efficiency in producing erythema (sunburn) in human skin. Quinone in 50% alcohol was photo-

lyzed behind this filter which was compensated, at each wave length, for the photochemical efficiency of this photolysis according to (unpublished) data by P. A. Leighton. Changes in total intensity and in spectral energy distribution are integrated by this device. The losses per hour in iodine value y were for seven carbon arcs, cored and uncored, plotted as ordinates against x , the reciprocals of times in which the same sources, without filters, produced a standard erythema. Roughly, $y = ax$. For the more efficient sources, $y = ax + b$ is preferable. The indicated threshold value will be further studied. Similar chemical actinometers for such purposes as photography, antirachitic therapy or even chlorophyll assimilation are possible.

CAMBRIDGE 38, MASSACHUSETTS

[A CONTRIBUTION FROM THE ALFRED LOOMIS LABORATORY OF TUXEDO, NEW YORK, AND THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES I. A PRELIMINARY SURVEY

BY WILLIAM T. RICHARDS AND ALFRED L. LOOMIS

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Introduction

Experiments on the production of sound waves for submarine signaling by a reversal of the Curie piezo-electric effect with quartz crystals in oscillating fields have been in progress for some time in several countries.¹ Since, however, the kinematic coefficient of viscosity increases as the square of the frequency, high frequencies would be absorbed rapidly in water, and these experiments have necessarily been conducted at relatively low frequencies. Recently one of us in conjunction with R. W. Wood² has shown that sound waves of great intensity may be similarly produced in high frequency fields, and that they are readily absorbed by liquids and solids. For this purpose a 2-kilowatt oscillator, capable of producing powerful oscillations with frequencies from 100,000 to 500,000 per second was employed; the quartz crystals, varying from 6 to 12 mm. in thickness and 50 to 80 mm. in diameter, were immersed in oil between two electrodes. The voltages used in submarine signaling are of the order of 1500, but the limiting voltage in our work is determined only by the sparking distance in oil between the two electrodes. In this way voltages of the order of 50,000 are possible and a corresponding increase in intensity of radiation is secured, since the amplitude of vibration

¹ A review of the literature on this subject is given in I. B. Krandall, "Theory of Vibrating Systems and Sound," McGraw-Hill Book Co., N. Y., 1926, p. 142.

² Wood and Loomis, *Phil. Mag.*, vii, 4, 417 (1927). This paper contains a comprehensive account of the physical and biological effects of supersonic waves, including detailed description of the apparatus for producing them.

of a quartz crystal increases directly with the voltage applied to it. The intense sound waves travel up through the oil into any vessel suspended in it.

Although no investigations on the chemical effects of compressional waves so produced have come to our attention, it is apparent that two correlated types of phenomena may be expected, and it is the purpose of this investigation to demonstrate their existence and order of magnitude. In the first place a series of standing waves set up by these vibrations consists of nodes and loops, matter in the nodes being relatively quiescent and in the loops being under varying tension. Therefore, at points of rarefaction in the standing waves, cavitation and similar phenomena involving the formation of a vapor phase are to be expected. Secondly, in the compressed regions of the standing waves an increase in kinetic energy density occurs, which corresponds to a local increase in temperature. Since the average temperature of the system is unaltered by this, the sound waves should have only an impalpable effect on the equilibrium constant of any chemical reaction. Such temperature changes should, however, affect the rate of a reaction, where temperature plays a considerable part, in so far as its temperature coefficient deviates from linearity, and a velocity constant corresponding to a higher temperature than that measured with a thermometer should be obtained. In the ordinary nearly balanced reaction, say the esterification of ethyl alcohol by acetic acid, it is possible that the increase in temperature of the condensed portion of the wave, and its corresponding increase in reaction velocity, would be so nearly balanced by the decrease in temperature in the rarefied portion that the measurable result on the reaction velocity would be negligible. On the other hand, in reactions which proceed irreversibly, or in any reaction extremely far from its equilibrium point, the gain in velocity of the condensed portion should not be offset by the loss in the rarefied portion, and the effect should be shown indisputably. It was a tentative argument of this kind which led to the experiments described below.

A third possible effect should be mentioned, although it cannot be treated in detail in this communication, namely, the effect of the vibration frequency of the sound wave itself on an unstable molecule, apart from its local kinetic effect upon molecules collectively. Although the frequencies used in the work described below (289,000 per second unless otherwise stated) were of a magnitude far below that of molecular vibration, certain effects, to be discussed later, seem to substantiate such an hypothesis.

General Effects

Many sensitive metastable systems are discharged by the sound waves in accordance with the foregoing discussion. Nitrogen tri-iodide is, for example, exploded when subjected to sufficiently intense radiation;

this cannot be produced by touching a watch glass containing the dried explosive to the radiated oil, but occurs only when the iodide, moist, is plastered on an "accumulator" of radiation—a fine filament drawn from the neck of an Erlenmeyer flask, the bottom of which is suspended in the radiated oil. Under these conditions the iodide collects in beads in standing waves in the glass filament, and is exploded progressively from the top to the bottom of the filament as it dries. Less sensitive explosives like ammonium nitrate, however, remain unaffected. Yellow mercuric iodide is converted to red below 120° by the sound waves, but the contact between the dry iodide and the glass is poor, and regular sound-patterns cannot be so produced. No other allotropic changes of those investigated (for example, sulfur, phosphorus, etc.) were sufficiently sensitive to give consistent results.

The sound waves have an explosively discharging effect on superheated liquids; carbon tetrachloride, for example, superheated 5° evaporates so violently as to half empty the test-tube which contains it. Similarly, carbon dioxide supersaturated in water is violently relieved, but without the spectacular consequences attendant upon the relief of superheating. Supersaturated solutions of crystalline solids in liquids and supercooled liquids are, on the other hand, little affected. A sirupy solution of sodium thiosulfate was discharged by radiation collected by an "accumulator," a metastable crystal modification being produced. A sugar "glass," liquid salol supercooled 30° , and similar solutions and liquids gave, however, no consistent results. This is easily understood when it is remembered that the effect favoring the relief of supersaturation is in this case only that corresponding to the increased probability of germ formation due to the rise in temperature in the compressional waves.

The effect of the radiation on the critical phenomena in ether was investigated in the hope that banded regions of opalescence would be produced just above and just below the critical point. A great difference in appearance rayed and unrayed was observed, the time of opalescence extending over a much greater period in the latter. During the instant when the critical point was being approached from above, mottled patterns of opalescence were unquestionably observed in the rayed tubes, but either the phenomenon was not sufficiently marked, or the interference pattern of the glass was too complex, to permit its assignation to standing waves. Cinematographic records have been made, and it is hoped that they will reveal greater regularity than the eye can perceive.

One further effect of a chemical nature is sufficiently marked to warrant special mention: namely, the "atomization" of a substance at a liquid or gaseous interface. In this way emulsions of metallic mercury in water were produced which reduce potassium permanganate and remain in suspension for several days. Similarly a test-tube of distilled water

clear to the Tyndall beam before raying, becomes faintly turbid after raying, due to small glass fragments which are "atomized" from the walls. Because of this the rays are of no value whatever for the coagulation of microscopic particles, even fairly coarse suspensions such as silver chloride precipitated in water remaining unflocculated on raying.

Certain more physical effects of the rays are also important from the point of view of the experiments detailed below. When a test-tube of liquid is suspended over the oil-bath in which the crystal is oscillating, the sound waves which rise through the oil pass through the walls of the test-tube into the liquid and are absorbed, heating it rapidly. They also set up standing waves in the glass which, by friction with the liquid, produce heat. Such heating changes the average or integral temperature by sound radiation, and must be carefully distinguished from the local temperature effects discussed above. This general heating affects the liquid as long as sound waves reach it; jacketing with ice and water diminishes the intensity of radiation which reaches a vessel but in no way diminishes the heating of the liquid by that portion which enters it. Any other thermostating device would be equally futile and, isothermal conditions being impossible, quantitative measurements in the sound waves can be made only by following the rise in temperature. Here, however, another peculiarity of the radiation intervenes. The compressional waves enter the mercury of an ordinary thermometer, setting up standing waves in the walls of the bulb, and causing it to read many degrees higher than the actual temperature in the liquid. Again, heat produced at the liquid-glass interface causes a rise in temperature greater than that in the surrounding liquid, which further invalidates any readings made during the progress of raying. A thermocouple is equally if not more ineffective for measuring temperature during raying, since heat is generated at the metal-liquid interface which causes a high local temperature (dependent largely on the viscosity of the liquid), and a lag in determining the true temperature after discontinuing the radiation which is greater even than that of a mercury thermometer. Thus a singular difficulty is encountered in quantitative work; it is impossible to work isothermally, yet no adequate measure of the temperature during radiation has been found. The methods of extrapolation and interpolation used below are not extremely satisfactory, but at least give the temperature at any instant within 0.1° .

Furthermore, when a vessel is immersed in the radiating oil-bath, its distance above the quartz crystal is of immense importance for the obtaining of reproducible results; when this distance is made an exact number of half wave lengths, standing waves are produced between the crystal and the bottom of the vessel which greatly increase the intensity of effect in the vessel. This is clearly illustrated by the following

results, obtained with a flat-bottomed beaker 5 cm. in diameter containing 50 cc. of water, which was lowered beneath the surface of the oil by a micrometer screw, being rayed at successive points in its descent.

TABLE I
THE RESONANCE EFFECT ON THE HEATING OF WATER

Distance from surface of oil in cm.....	0	0.164	0.218	0.246	0.310	0.385	0.447	0.492	0.556
Rise in temperature for 30 seconds raying.	2.7	2.2	0.85	1.5	2.2	2.0	0.8	0.6	1.5

This series of observations gives a value for the velocity of sound in oil at a frequency of 281,000 per second of 1420 meters per second, probably the only determination at anything like this frequency which was in existence at the time it was made. Recently J. C. Hubbard and one of us³ have utilized a similar principle to measure very exactly the velocity of sound in liquids.

Since, therefore, the amount of heating in the liquid is not exactly determinable, and since it is affected by the frequency of the oscillating circuit which is changed by the temperature of the quartz crystal, by the heating of the oil, by the height and configuration of the vessel, and even perhaps by the pressure hysteresis of the vessel, the reproduction of quantitative results by magnitude rather than by percentage error has alone been attempted in the sections which follow. A large test-tube with a hemispherical bottom has been found to minimize many of the sources of error outlined above, since it bridges several half wave lengths, and hence is almost devoid of tuning effects, but loses of course, in consequence, some of the energy of the waves by interference. It has been used wherever possible below.

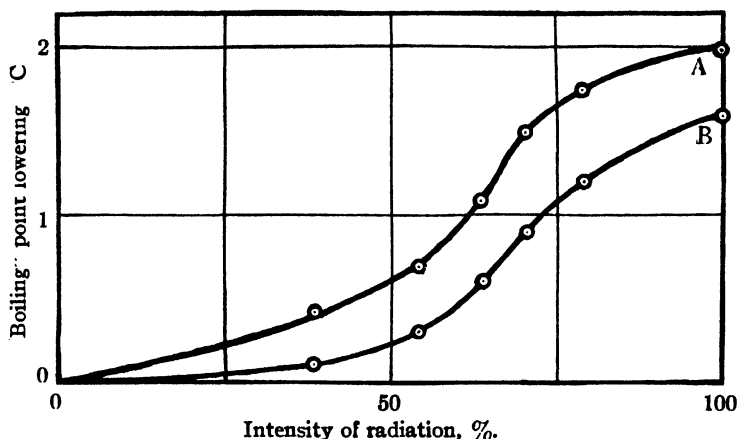
The Lowered "Boiling" Temperature of Liquids

Preliminary measurements showed that, besides relieving superheated liquids, the sound waves would produce bubbles of vapor in air-free liquids at about 1° below their boiling temperature. Results of this kind were obtained with water, toluene, carbon tetrachloride and ether. It became, therefore, of interest to investigate the magnitude of this effect and its variation with the intensity of radiation.

Water and carbon tetrachloride were selected because of their ease of purification, chemical and associative dissimilarity and non-inflammability. A number of devices to secure slow cooling from the boiling point of these liquids were tried, the most satisfactory being jacketing the tube under observation with a spaced cage of German silver wire through which a voluntarily variable current was passed. In this way temperatures in the neighborhood of the boiling point of the liquid could be maintained to $\pm 0.05^\circ$ for several minutes. These were read by a thermometer held in the tube with a cork, through which passed also a ring stirrer to insure even heating throughout the liquid.

³ Hubbard and Loomis, *Nature*, 120, 189 (1927).

At a given temperature, the stirrer was clamped above the surface of the liquid to prevent local frictional heating, and the tube was lowered into the oil while the latter was being radiated with a predetermined intensity. The liquid had of course been scrupulously freed from dissolved gases by boiling. If bubbles of vapor at once appeared in the center of the tube, which was illuminated by a powerful beam of light to facilitate observation, the liquid was considered to "boil." If bubbles appeared only after five seconds it was considered not to "boil." The temperature was then readjusted and the observation repeated. Ten trials fixed the lowest temperature for which water would "boil" with a given intensity of radiation within $\pm 0.05^\circ$, with carbon tetrachloride within $\pm 0.10^\circ$. The intensities of radiation were determined by the heating effect of thirty seconds of radiation upon 25 cc. of water in a test-tube at 25° , the voltage in the oscillating circuit being altered at will. A relative intensity of 100% heated 25 cc. of water 2.8° , and 25 cc. of carbon tetrachloride 5.2° in thirty seconds.



A, carbon tetrachloride; B, water.

Fig. 1.—The lowering of the "boiling" point of water and carbon tetrachloride at atmospheric pressure by high-frequency sound waves as a function of the relative intensity of the radiation.

The results of this series of measurements are given below and are plotted in Fig. 1.

TABLE II

THE EBULLITION OF AIR-FREE WATER WITH VARIOUS RADIATION INTENSITIES AT ATMOSPHERIC PRESSURE

Relative intensity, %.....	100	79	70	63	54	46	40	0
"Boiling" point of water.....	97.8	98.2	98.5	98.8	99.1	99.2	99.3	99.4
"Boiling" point of CCl ₄	75.1	75.3	75.6	76.0	76.4	76.7	..	77.1

The actual boiling point at atmospheric pressure (0% intensity) was determined in the vapor of the liquid in a distilling flask, the barometric pressure being for the water determinations 744.8 mm. and for the carbon tetrachloride 743.5 mm.

In the hope of facilitating the interpretation of these results, measurements were also made in a very similar apparatus with air-free water

and carbon tetrachloride hermetically sealed under their own vapor pressures. The results for carbon tetrachloride were not reproducible, a lowering in the ebullition point of about 15° being observed for 100% intensity. Those for water were reproducible to $\pm 1.0^\circ$, but are not very satisfactory for the interpretation of the phenomenon since the exact point at which, under these conditions, water ceases to boil under its own vapor pressure is not clear.

TABLE III

THE EBULLITION OF AIR-FREE WATER UNDER ITS OWN VAPOR PRESSURE

Relative intensity, %.....	100	79	70	63
Temperature of ebullition.....	51.0	53.5	57.0	61.0

With lower intensities the results were scattered, an intensity of 30% producing no ebullition at 85° , a temperature far above 63° where ebullition could still be produced by jarring the tube without supersonic waves.

The interpretation of these results is difficult and can be attempted only tentatively. The falling off of the effect on the ebullition point with increasing intensity above 70% means, owing to its method of measurement, only that the heating effect of the waves increases more than their vapor-forming effect. That the function is of the same type in both cases plotted in Fig. 1 suggests that with increasing intensities complex interference patterns are set up in the vessel employed, and more of the radiation heats the liquid from contact with the walls, while less enters it to effect vaporization per unit rise in temperature of the system. This agrees with the qualitative observation that sound patterns on glass plates are best developed with low radiation intensities. The "boiling" point lowering of carbon tetrachloride is less than its greater heating effect per cubic centimeter would lead us to expect at high intensities, for carbon tetrachloride is raised in temperature 1.8 times as much as water, and $1.8 \times 1.6^\circ = 2.9^\circ$, whereas the "boiling" point lowering in carbon tetrachloride at 100% intensity is only 2.0° .

In attempting to discuss the significance of the results it must clearly be borne in mind that, as has been already indicated, sound waves hardly can produce a general effect on physical equilibria in such a system as water-water vapor, and hence that all explanations must be referred to local variations in the properties of the liquid in standing waves. Unfortunately the vapor pressure changes corresponding to different intensities in the three cases quoted above have no uniformity, and the fundamental mechanism of the local phenomenon must be left undetermined. Arguments of about equal weight may be advanced that this "boiling" takes place in the compressional or in the rarefied portion of the wave. In the former the temperature is higher and the pressure more intense; these changes tend to produce boiling in the liquid since both raise its vapor pressure.

Also, at a higher temperature, the surface tension of the liquid is diminished, making it easier to form a bubble of vapor which is not redissolved; this effect is probably negligible at atmospheric pressure, but seems to become very important when the liquid "boils" under its own vapor pressure. On the other hand, in the rarefied portion of the wave the liquid is under tension, which would tend to produce cavitation and the formation of vapor at less than atmospheric pressure. In this region, however, the temperature is lower, the surface tension higher, and the tendency of the vapor to form therefore diminished. No data are at hand to decide which of these two effects produces the result and we must be content with the statement that they cannot reinforce each other. If the former is effective, the artificial "boiling" may be said to be equivalent to actual local boiling, since the vapor is liberated at something more than atmospheric pressure; if the latter, the "boiling" must be considered merely a low-pressure ebullition. The sole observation which enables a choice to be made is that the bubbles rise, slowly diminishing in size to the surface through 5 cm. of liquid, and are hence probably at not less than atmospheric pressure, but this can by no means be considered conclusive evidence.

The Expulsion of Gases Dissolved in Water

A flask of water at 25° which has previously been saturated with air at 30° and then tightly stoppered becomes, upon being radiated, at once filled with bubbles of gas released by the sound waves. Similar results are obtained when the air-saturated liquid is carbon tetrachloride, methyl or ethyl alcohol, benzene, etc. Measurements were made to demonstrate the reality of this effect and the conditions which govern it.

The vessel in which the gases were liberated was constructed from a 200cc. Pyrex Erlenmeyer flask. A vertical side tube, goose-necked, and containing a small capillary constriction, was attached to this about half-way down its side, and a ring seal blown in the neck which projected a small bore test-tube almost to the bottom of the flask. This ring seal was sloped so that any gas caught under it would collect at a single point and at this point was sealed a stopcock. The volume of the flask was then measured from the under side of the barrel of the tap to the beginning of the capillary constriction. In filling the vessel with liquid to be rayed it was first dried and brought to the temperature of the thermostat, and the air which it contained swept out by the saturating gas under observation. It was then filled from a reservoir of gas-saturated liquid at the same temperature and, all bubbles of gas having been excluded, was rayed until its temperature, measured with a tested accuracy of 0.03° by a thermometer immersed in a little water in the test-tube set in the neck, had risen an appropriate amount. The gas liberated collected below the tap and was ejected into a gas buret of the usual type which gave its volume to 0.01 cc. Knowing the solubility-temperature function of the gas in the liquid under ordinary conditions, the saturation temperature and pressure, the final temperature after raying, the conditions under which the volume of the gas had been measured, and the volume of the flask, it was easy to calculate the amount ejected by supersonic rays in excess of that corresponding to the decreased solubility

of the gas due to the temperature rise. The only serious experimental difficulty in the procedure was that the sound waves occasionally produced vibrations in the flask which shattered it.

The saturating gases were nitrogen and oxygen, used from "air refined" tanks without especial purification. The water was saturated by bubbling at atmospheric pressure minus the pressure of aqueous tension at 30.2° in a large thermostat. It was demonstrated chemically that three hours' bubbling was necessary to free previously air-saturated water from all but 0.5% of its oxygen by nitrogen bubbling, hence the liquid was not considered suitable for use until at least this time had elapsed during the bubbling process.

The results obtained are given in Table IV.

TABLE IV
THE EFFECT OF RADIATION ON GASES DISSOLVED IN WATER

Oxygen saturated at 30.2°, 744 mm. barometric pressure						
Determination number		1	2	3		
I	Volume of vessel, cc.....	201	201	201		
II	Temperature after raying, °C.....	39.3	37.0	34.5		
III	Cc. of gas evolved (N. T. P.).....	1.52	1.45	1.24		
IV ^a	Cc. of gas corresponding to solubility	0.65	0.51	0.30		
V	Expelling factor of rays (III/IV).....	2.3	2.8	3.7		

Nitrogen saturated at 30.2°, 743 mm. barometric pressure						
Determination number		4	5	6	7	8
I	Volume of vessel, cc.....	200	200	200	201	240
II	Temperature after raying, °C.....	38.6	36.8	39.3	36.6	36.6
III	Cc. of gas evolved.....	0.93	0.71	0.94	0.71	0.84
IV ^a	Cc. of gas, theoretical....	.33	.27	.33	.26	.31
V	Expelling factor (III/IV).	2.8	2.6	2.8	2.7	2.7

^a The figures given after IV were obtained from the generally accepted results of Winkler for the solubilities of nitrogen and oxygen in water, and represent the difference between the volume of gas dissolved in the volume of water in question at the lower and at the higher temperature. V therefore represents the ratio between the volume of gas obtained and that calculated on the assumption that the sound waves would have no other effect than perfectly to relieve supersaturation resulting from the rise in temperature.

Each flask of different volume in the nitrogen determinations differed in type and weight. All determinations were made at 100% intensity except No. 9, which was at 70%. The constancy of the "expelling factor" for nitrogen indicates that the gas is uniformly given off throughout the period of raying and that the size and shape of the vessel and the intensity of the radiation do not affect the phenomenon; the effect of these variables has, however, been tested only over a limited range. The variations in this factor for oxygen are due to other causes.

Similar observations with carbon dioxide in water gave positive but quantitatively unsatisfactory results owing to the great solubility of the gas. With air in water the results consistently presented an interesting anomaly which will not be considered in this communication.

These measurements may be more easily interpreted than those discussed in the foregoing section, since small variations in the properties of the solvent should not, in this case, influence the result. The phenomenon may, therefore, be considered one of cavitation in the tensional regions of the standing waves, a pressure lower than atmospheric being produced locally which causes the dissolution of the gas. Therefore, it cannot be considered that the solubility of the gas is diminished in the thermodynamic sense, but only that in certain regions in the liquid conditions deviating from the average ("equilibrium") conditions are produced which cause the expulsion of gas bubbles which, rising through the liquid, are not considerably redissolved.

The Acceleration of Chemical Reactions

The purpose of this section is to demonstrate that certain chemical reactions when radiated by sound waves proceed more rapidly than is to be inferred from a strict consideration of their thermometric or integral temperature. The reactions studied must evidently be homogeneous liquid reactions since gases conduct the waves very little at ordinary pressures and solids, especially powders, are unreliable conductors. Electrometric measurements being difficult because of the exceedingly high voltages in the immediate neighborhood of the reaction under observation, the field for preliminary investigation is further narrowed to time reactions with a visual end-point, that is, "clock" reactions. A conclusively positive effect was obtained with two of the three of these which were studied.

The first, the induction period of the reduction of potassium permanganate by oxalic acid was unsatisfactory. The end-point, when the reaction was adjusted to be slow enough to allow radiation for one minute, was indefinite. Any effect of the radiation was therefore within the limit of error of observation.

The second reaction employed a familiar principle in a manner which had not come to our attention; it will later be described in detail by one of us. Dimethyl sulfate was hydrolyzed in basic solution in the presence of an indicator, in this case "brom-thymol blue." The solution contained only enough base to neutralize a quarter of the sulfuric acid liberated by hydrolysis and consequently, when neutralization had taken place, a sharp change in hydrogen-ion concentration (roughly from P_H 8 to P_H 3) occurred in a very few seconds, and the indicator was almost instantaneously changed in color. This reaction is especially satisfactory for the work in hand because it is easily adjustable to a wide range of reaction times, because it is not affected by oxygen in the air, and because the gradual inevitable heating due to sound waves caused the end-point only to become more sharp. The most satisfactory concentrations of constituents were obtained by adding 2 cc. of dimethyl sulfate to 100 cc. of 0.01 *N* sodium

hydroxide strongly colored with neutral "brom-thymol blue." Under these conditions the end-point of the reaction was reached in 335 seconds at 23.0°, 155 seconds at 30.2° and 82 seconds at 35.3°, the end-point of a single determination being clear ± 3 seconds at the lower temperature and ± 1 second at the higher.

In order to determine the effect of raying, the reaction was begun in a flask and as quickly as possible transferred to two scrupulously cleaned test-tubes, one of these being subjected to radiation at zero time. The other, used as a control, was simultaneously dipped into a bath of water at about 50° and held there, vigorously stirred, for a measured length of time just sufficient to bring its temperature above that of the rayed sample after 15 seconds' radiation. After radiation had been discontinued, the next 15 seconds were occupied in ascertaining the temperature of both portions of the solution with compared thermometers. Raying was then resumed for 15 seconds with one sample while the control was again warmed to follow the new rise in temperature. The process was continued until the blue color of the indicator became suddenly yellow in both, when the total time for each was recorded. By practice it became possible to follow with the control the temperature of the rayed sample within a few tenths of a degree, keeping the former always slightly higher in temperature to make temperature errors adverse to the effect desired.

A complete temperature-time picture of two parallel rayed and unrayed samples is given graphically by curve A, Fig. 2. This represents Determination 2, Table V; by a study of this chart the method of reporting the reactions will become sufficiently clear.

TABLE V

THE EFFECT OF SOUND WAVES ON THE HYDROLYSIS OF DIMETHYL SULFATE

Determination 1. Starting temperature, 20.4°

Temperature rayed, °C.....	24.7	26.9	28.6	30.8	32.6	34.4	36.2
Temperature unrayed, °C.....	23.8	26.1	28.5	31.0	33.2	35.0	36.2
Immersion of unrayed, seconds.....	4	11	12	14	16	14	15

Reaction time rayed, uncorrected, 195 seconds; corrected to 30.0°, 177 seconds.

Reaction time unrayed, uncorrected, 195 seconds; corrected to 30.0°, 178 seconds.

Determination 2. Starting temperature, 22.5°

Temperature rayed, °C.....	22.9	24.9	27.0	29.0	30.8	32.4	34.0
Temperature unrayed, °C.....	23.2	25.4	27.8	30.2	31.4	32.4	34.0
Immersion of unrayed, seconds....	3	5	8	7	4	6	13

Reaction time rayed, uncorrected, 195 seconds; corrected to 30.0°, 204 seconds.

Reaction time unrayed, uncorrected, 193 seconds; corrected to 30.0°, 218 seconds.

Only two determinations are reported since they represent the most conclusive and the most inconclusive results obtained, and the space which they require is disproportionate to their importance. In Deter-

mination 1 the effect of raying is within the limit of error of observation and the result must be considered doubtful. In the other an acceleration by raying has been obtained, as is made clear by the corrected reaction time value at 30.0° . This was obtained by use of the temperature coefficient, the data for which are given above, on the assumption that it is independent of concentration over a small range, and by use of the approximation that over 2° intervals the temperature-reaction-time function is linear. Because both these simplifications are entirely reasonable, and because, moreover, any errors introduced by them affect equally

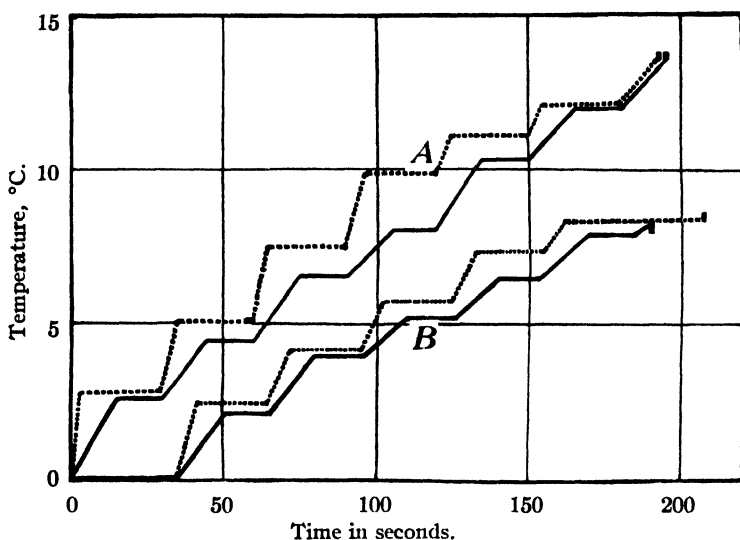


Fig. 2.—A temperature-time picture of two reactions accelerated by sound waves. *A* represents the hydrolysis of dimethyl sulfate, *B* the iodine "clock" reaction; in each case the temperature of the unrayed control solution is indicated by a dotted line. The starting temperature of *A* was 20.4° , of *B* 23.8° .

the control and the rayed portion of the solution, it is estimated that the reaction times corrected to 30.0° are accurate to better than 1%. The acceleration of the reaction, averaged from all results, was 10 seconds at 30.0° .

It is perhaps disappointing that no more conclusive uniformity in the accelerating effect of the sound waves is here observed. To account for the divergence of the results it is only necessary, however, to recall the great difficulties encountered in reproducing the experimental conditions in any two parallel determinations.

The third reaction observed was the long familiar iodine "clock" depending upon the reduction of potassium iodate by sulfurous acid. This gave a much more clearly positive, although more difficultly interpretable,

result. Solutions 0.01 *M* to KIO_3 and 0.0164 *M* to Na_2SO_3 were prepared, the latter being made 4.6×10^{-4} *N* in sulfuric acid and containing also a suitable quantity of boiled starch. At a given instant 25 cc. of iodate solution was mixed with 55 cc. of sulfite solution, both at a measured temperature, and thoroughly shaken. After mixing the solution was at once poured into two large scrupulously clean test-tubes, and one of them subjected to 15 seconds' radiation while the other was externally warmed. The tubes were subsequently treated exactly as in the study of the previous reaction. The results obtained are reported in Table VI.

TABLE VI
THE EFFECT OF SOUND WAVES ON THE IODINE "CLOCK" REACTION

Detn. no.	Rel. intens., %	Time elapsed before raying, seconds	Temp. at start, °C.	Average temp. during raying, °C.	Final temp., °C.	Time end-point reached, seconds
1a	100	45	23.5	26.8	29.5	190
1b	0			29.0	34.0	210
2a	100	55	25.0	27.7	30.1	190
2b	0			28.7	31.4	205
3a	100	45	24.0	28.2	32.1	190
3b	0			29.6	33.5	210
4a	100	55	25.0	28.2	31.2	188
4b	0			28.9	33.3	207
5a	100	40	25.0	29.1	33.0	188
5b	0			30.0	34.1	203
6a	70	45	25.0	27.7	29.9	180
6b	0			28.6	31.0	206
7a	70	40	24.5	27.1	29.4	183
7b	0			27.7	30.0	208
8a	54	40	25.0	26.8	28.4	190
8b	0			27.8	28.6	215
9a	0	30	24.5	..	25.2	222
9b	0			..	25.5	224
10a	40	30	23.8	25.6	27.1	204
10b	0			26.3	27.5	227
11a	100	34	23.8	28.1	32.1	190
11b	0			28.5	32.1	207
12a	57 ^a	41	24.5	26.5	28.6	192
12b	0			26.9	28.9	214

^a This determination was carried out at a frequency of 324,000 per second, all others being at 289,000 per second.

In this table the *a* determinations have been subjected to radiation and the *b* determinations heated to follow their rise in temperature. A temperature-time picture of Determination 11 is presented graphically in Curve B, Fig. 2; here the time that elapsed before radiation was begun has also been plotted to give a complete picture of the reaction. Determination 10 was subjected to six 15-second periods of raying, and the other determinations each to five 15-second periods. The measurements

included in Table VI are representative of over thirty similar observations made. In no case were anomalous results observed which are not represented in the table. Number 9 of these determinations is a very important check upon the general conditions of the reaction; it was carried out exactly as the others except that the tube containing the radiated sample barely touched the radiated oil, and the intensity of sound waves entering it was therefore negligible, the slight heating effect observed being due only to the fact that the oil temperature was about 30°. This determination eliminates at once the possibility that the reaction is accelerated by the high frequency field.

It is unnecessary to apply a correction for the difference in temperature between the rayed and unrayed solutions in these measurements, and hence individual heating curves have been averaged during the period of raying. The temperature coefficient of this reaction is abnormal, varying considerably with the concentrations of the components. The reaction times of these solutions were 244 seconds at 20.7°, 188 seconds at 30.2° and 174 seconds at 33.1°. Since this function is nearly linear and its slope very abnormally low, the small difference in temperature between the two solutions affects their reaction times only by a factor of the second order. Since each control is at all times kept slightly above the temperature of the corresponding rayed solution, acceleration of the latter due to temperature errors is impossible, and the results are most clearly reported as they were actually observed.

Several aspects of this reaction, in contradistinction to that preceding it, strongly suggest that a factor much more powerful than the mere deviation of its temperature coefficient from linearity is involved. In the first place, the temperature coefficient of the reaction is abnormally low, a change from 25° to 35° decreasing the time by only about 25%. Furthermore, the lack of variation of the accelerating effect with intensity of radiation is exceedingly puzzling if the higher temperature of the condensed region alone is the activating agent. Finally, the excessively large effect upon the reaction velocity in comparison with that of the hydrolysis of dimethyl sulfate, and its far greater reproducibility, at once suggest a difference in action in the two cases. As a tentative explanation for these phenomena it does not seem unreasonable to suppose that the frequency of the sound waves themselves had a disintegrating effect upon some compound found in the complex chain of reactions which led to the ultimate liberation of iodine. In order to test this hypothesis Reaction 12 was carried out at a higher frequency, no quartz crystal of lower being readily available. The results show that if frequency of vibration is a determining factor it is a "band" rather than a "line" effect, but this does not in the least invalidate the hypothesis. A systematic potentiometric investigation into the stability of the various com-

pounds involved in this reaction and of other unstable molecules under sound radiation of various frequencies will at once be undertaken. In this field, as well as in several others which we can only suggest in so cursory a survey of the chemical phenomena produced by high frequency sound waves, we hope to obtain further information in the near future.

Summary

It has been demonstrated that intense high frequency compressional waves produce certain chemical effects, especially discharging metastable systems of great sensibility. They furthermore expel gases from liquids, cause ebullition in pure liquids at temperatures considerably below their boiling points at atmospheric pressure, and accelerate certain chemical reactions. The conditions of intensity and frequency affecting these phenomena have been considered. The reasons for this action are discussed, tentative explanations for various anomalous effects being advanced.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VI. THE PHOTOCHEMICAL REACTION BETWEEN OXYGEN AND MERCURY VAPOR AT RELATIVELY LOW PRESSURES

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The fundamental researches of Cario and Franck,¹ which showed that active hydrogen is produced by the illumination of a mixture of hydrogen and mercury vapor with the resonance radiation of mercury, have led to many interesting results in photochemical work. Nearly all of the reactions studied have involved hydrogen or molecules containing hydrogen atoms.

Dickinson and Sherrill² have shown that ozone is formed when a mixture of oxygen and mercury vapor is exposed to the resonance radiation of mercury in a dynamic system. They also observed the formation of a brown deposit which they assumed to be mercuric oxide. It is difficult to make determinations of the quantum efficiencies of reactions involving the resonance radiation of mercury due to the exceedingly small width of the absorption line of mercury vapor at $253.7m\mu$, but Dickinson and Sherrill showed that at least seven molecules of ozone were produced per mercury atom passing through the reaction vessel.

The present work was started with the object of ascertaining whether

¹ Cario and Franck, *Z. Physik*, **11**, 161 (1922).

² Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

mercuric oxide is formed as a primary process in the reaction between oxygen molecules and excited mercury. The results to be reported conflict in no way with the findings of Dickinson and Sherrill and will, it is hoped, throw some light on the mechanism of the pressure decrease accompanying the photochemical reaction of oxygen with mercury vapor.

I. Experimental Procedure and Results

The oxygen used in these experiments was prepared by heating solid potassium permanganate. It was dried by standing over phosphorus pentoxide.

No stopcocks were used in the main apparatus. The only source of impurity of this sort would be the wax used to attach the window to the reaction vessel. In most of the experiments a special vacuum wax was used. The edge of the vessel was well ground and the windows were plane so that relatively little surface of wax was exposed. In order to obtain evidence as to the possible effect of the wax, sealing wax was used in part of the experiments with no noticeable change in results.

Previous to making a run the vacuum system was always evacuated for several hours with continual flaming of all parts except the reaction vessel proper. Due to the wax the reaction vessel could not be heated.

The window was of plane, transparent, crystalline quartz. To eliminate the short wave lengths two different varieties of special glass were used. The first of these showed no transmission below $245\text{ m}\mu$ when photographed with a quartz spectrograph, even with a relatively long exposure. The transmission of this glass was obtained with the use of the quartz spectrograph and rotating sector. It showed approximately 50% transmission at $253\text{ m}\mu$. The second glass showed faint transmission as far as $230\text{ m}\mu$ and a somewhat greater transmission than the other variety at $253\text{ m}\mu$. In addition it showed only extremely faint transmission in the visible spectrum for wave lengths longer than $440\text{ m}\mu$. Both of these glasses eliminated those wave lengths which cause direct, unsensitized ozone formation and in addition the second of the two absorbed most of those radiations in the visible spectrum which cause ozone decomposition.³

The quartz mercury arc lamp was made in the laboratory. The arc played in a tube about 5 mm. in diameter. In most of the experiments the arc was operated under water. One series of experiments was made with the warm arc. However, the reversal of the $253.7\text{ m}\mu$ line is not complete in an arc of this type and, moreover, the general characteristics of the spectrum changed when the arc was allowed to warm up, so that in the final runs partial reversal of the resonance radiation was obtained in two different manners: (1) by interposing a cylinder open to the air at both ends, but containing a ring of liquid mercury at the lower end; (2) the apparatus shown in Fig. 1 was adopted in most of the runs. The reaction vessel is represented by D. A is a quartz window about 3.5 cm. in diameter while B is a second quartz window about 3.0 cm. in diameter. C is connected to the McLeod gage and to the vacuum pumps. E is connected to the vacuum pumps through the trap F. The trap could be isolated from the main apparatus by means of a mercury cut-off. The quartz mercury arc lamp was placed below A and the level of water is shown by the dotted line.

It is difficult to make an exact estimate of the extent to which the intensity of the $253.7\text{ m}\mu$ is reduced by the method used. Wood⁴ has stated that mercury vapor at room temperature (which he gives as 22°) reduces the intensity of the resonance radiation of mercury by 50% in a distance of 5 mm. He states that a simple exponential

³ Griffith and Shutt, *J. Chem. Soc.*, 119, 1948 (1922).

⁴ Wood, *Phil. Mag.*, 23, 689 (1912); *Physik. Z.*, 13, 353 (1912). The recent work of Hughes and Thomas [*Phys. Rev.*, 30, 466 (1927)] agrees approximately with this work.

law is not exactly followed, but that it may be used approximately for thicknesses of mercury vapor up to one or two centimeters. This absorption line of mercury vapor should be broadened by the presence of foreign gases. However, the oxygen used in these experiments was at sufficiently low pressure so that little effect of this sort would be noticed. Nevertheless a few runs were made in which nitrogen at a pressure of six or seven centimeters was admitted to the absorption cell E. Theoretically this addition of nitrogen should produce a slight effect, but this seemed to be less than the experimental error. The thickness of mercury vapor traversed by the radiation was about 2.1 cm. The temperatures used in these experiments were slightly higher than 22°, but if calculations based on the above figures are made the intensity of the resonance radiation of mercury should be reduced by 90 to 95% by the arrangement described. When reversal of the resonance radiation was not desired the trap F was immersed in liquid air.

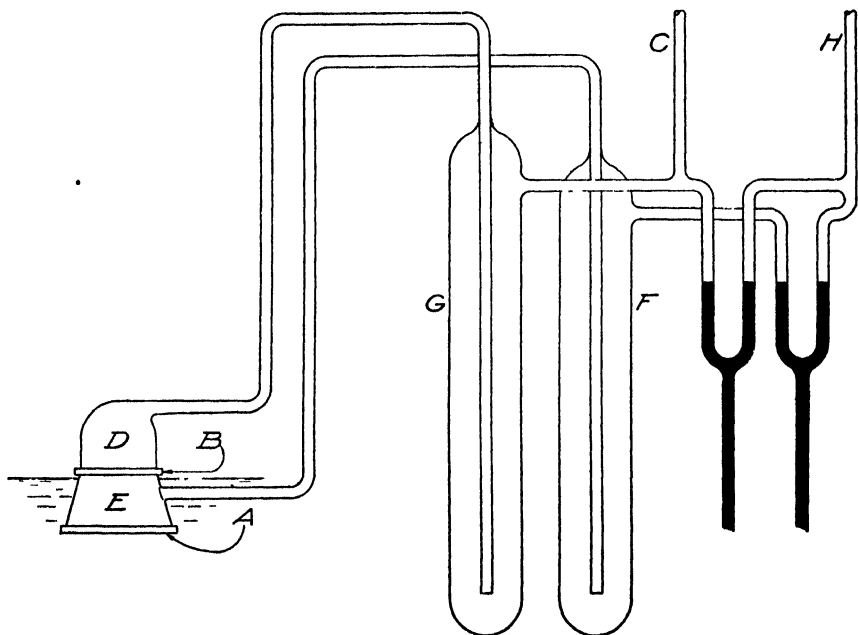


Fig. 1.

Liquid mercury in the reaction system was about a meter distant from the reaction vessel. The vapor pressure of the mercury was that at room temperature in most of the experiments. In a few of the experiments it was lowered by immersing the trap G in an ice-water mixture.

Exact calculations based on pressure change are impossible due to the fact that the quartz window became covered with a film. This film when dissolved in nitric acid showed characteristic tests for mercury with hydrogen sulfide and with a copper wire. Since the mercuric oxide was deposited on the window and on the walls for a distance of 1.0 to 1.5 cm. from the window, this is evidence that the resonance radiation of mercury is important.

With the experimental devices described, it was possible to carry out the following series of experiments.

A. The reaction between mercury vapor and oxygen in the presence of radiation from the cooled mercury arc, that is, with radiation which causes direct ozone formation and the resonance radiation of mercury both present.

B. In the presence of radiation from the cooled mercury arc with the exception of radiation which causes direct (unsensitized) ozone formation.

C. In the presence of radiation from the cooled mercury arc with the exception of the resonance radiation which was partially reversed.

D. In the presence of radiation from the cooled mercury arc with the exception of the resonance radiation of mercury which was partially reversed and the radiation which causes direct ozone formation.

The following tables show various examples of the data obtained. Due to the fact that the mercuric oxide film caused a gradual decrease in the intensity of the radiation, only those values listed together should be compared.

TABLE I
EFFECT OF MERCURIC OXIDE FILM ON REACTION RATE

Time, min.	Pressure of oxygen, mm.	$\frac{dp}{dt}$, mm./min. $\times 10^4$	Experimental conditions
0-100	0.1986-0.1834	1.52	Full radiation from cooled mercury arc
150-200	.1768- .1703	1.30	
300-350	.1602- .1562	0.80	
500-550	.1468- .1438	.60	
1000-1100	.1248- .1230	.18	

TABLE II
EFFECT OF ELIMINATING SHORT WAVE LENGTHS AND OF PARTIAL REVERSAL OF THE RESONANCE RADIATION

Time interval, min.	Pressure of oxygen, mm.	$\frac{dp}{dt}$, mm./min. $\times 10^4$	Experimental conditions
136	0.2226-0.2196	0.221	Full radiation
685	.2196- .2192	.006	Without wave lengths shorter than 245 $m\mu$
205	.2192- .2161	.151	Full radiation
365	.2161- .2159	.005	Without wave lengths shorter than 230 $m\mu$ and visible radiation
60	.2159- .2146	.217	Full radiation
645	.2146- .2119	.0419	Full radiation except with partial reversal of 253.7 $m\mu$
650	.2119- .2049	.108	Full radiation
800	.2049- .2025	.030	Full radiation except with partial reversal of 253.7 $m\mu$
120	.2105- .2105	.00	Full radiation from warm arc without wave lengths shorter than 245 $m\mu$

The data given in the tables are examples chosen from a large number of runs. The effect of eliminating the short wave lengths is practically to stop the reaction, in many cases the change in pressure being less than the experimental error. As the average of a large number of determinations, it is found that the reaction rate with the short wave lengths absent is about 3% of the reaction rate with the full mercury arc. The results with partial reversal of the resonance line are somewhat less constant, but the average of a large number of determinations shows that the reversal of the resonance radiation reduces the reaction rate to approximately 25% of the rate obtained with the full mercury arc.

II. Discussion of Results and Conclusions

We may summarize the results obtained in the following table if the reaction rate with radiation from the full cooled mercury arc is taken as 100 and the intensity of each part of the spectrum is expressed in per cent. of radiation from the cooled mercury arc.

TABLE III
SUMMARY OF RESULTS

Approximate intensity of resonance radiation, %	Approximate intensity of short wave lengths, %	Relative reaction rates
100	100	100
50	0	3
10	100	25
10	0	0

The ionization potential of mercury vapor is 10.4 volts, while the resonance potential is 4.9 volts. The ionization potential of excited mercury vapor should be 5.5 volts. If the formation of mercuric oxide involves the transfer of electrons from the mercury to the oxygen, the reaction between excited mercury and normal oxygen should take place if molecular oxygen has an electron affinity of the proper magnitude. The work of Gibson and Noyes⁵ indicates that molecular oxygen does not have a pronounced tendency to pick up electrons. That the reaction between excited mercury and normal oxygen to form mercuric oxide is not appreciable is indicated by the above results.

The results described indicate fairly definitely that the reduction in pressure in the system is to be ascribed to a reaction between mercury vapor and ozone. Ozone may be formed in the system by two methods, viz., by the direct unsensitized reaction and by the action of excited mercury and oxygen as indicated by Dickinson and Sherrill.² However, the quantity of ozone present in a static system when a mixture of mercury vapor and oxygen is illuminated with the resonance radiation of mercury must be exceedingly small since the reaction rate is practically zero under these conditions.

⁵ Gibson and Noyes, *THIS JOURNAL*, **43**, 1255 (1921).

At a first glance it might seem that the reaction is largely between excited mercury and ozone. A simple calculation based on kinetic theory shows that the average time between collisions of a mercury atom with oxygen is of the order of 10^{-6} second. Since the duration of mercury in the excited state is of the order of 10^{-7} second⁶ and the pressure of ozone in the system is certainly small compared to the pressure of the oxygen, it would appear that collisions between excited mercury and ozone would be exceedingly rare. It might be possible to avoid this difficulty by postulating an intermediate complex of some sort with relatively long life, or by ascribing a large diameter to excited mercury atoms. The latter assumption would necessitate the additional assumption of low efficiency of collision between excited mercury and oxygen.

It is possible to show that, if the short wave lengths and the 253.7 m μ line act independently and the effects of the two types of radiation are additive, the reaction rate due to resonance radiation must be proportional to about the fourth power of its intensity. This is an unreasonable value. It seems necessary to conclude, therefore, that there is some interaction between the products formed by the radiation of short wave length and the products formed by the action of the resonance radiation. It can be shown that the reaction between excited mercury and ozone to produce mercuric oxide and two atoms of monatomic oxygen is thermodynamically possible. The result of this reaction would be to increase the rate of formation of ozone in the system.

Dickinson and Sherrill² consider that activated oxygen molecules (or perhaps monatomic oxygen) may be formed by the interaction of excited mercury with oxygen. It is probable that the action of the short wave lengths is to produce activated oxygen molecules which may dissociate upon collision.⁷ It does not seem possible at the present time to ascertain whether these two types of activated molecules would be at all similar. Since the heat of dissociation of oxygen is now considered to be approximately 160,000 calories per mole, active mercury atoms would only be able to dissociate oxygen under exceptional circumstances due to a deficiency of some 45,000 calories per mole in energy content. However, it may not be unreasonable to expect a temporary combination of the nature of a mercury peroxide, for oxygen is paramagnetic, a fact which has led Lewis to conclude that the structure of the oxygen molecule may be represented by the formula $:\ddot{O}:\ddot{O}:$.⁸ This sort of compound would in all probability

⁶ See Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Company, New York, 1927, p. 176-177.

⁷ See Franck, *Trans. Faraday Soc.*, 21, 536 (1926); Birge and Sponer, *Phys. Rev.*, 28, 250 (1926). This applies, of course, to those wave lengths longer than the region of continuous absorption (below 175 m μ).

⁸ Lewis, *Chemical Reviews*, 1, 231 (1924); *THIS JOURNAL*, 46, 2027 (1924).

be analogous to such unstable compounds as Hg_2 and Na_2 , which Franck⁷ considers to be formed only when one of the atoms entering into combination is in the excited state. If the formation of such a complex is postulated, ozone may result upon collision of the complex with oxygen, or perhaps a larger amount of ozone upon collision of the complex with an activated oxygen or an ozone molecule. This would offer an explanation of the results herein reported. It is not possible, however, to draw such conclusions with entire certainty, as other conclusions may appear more plausible to various workers in this field. Lind and his co-workers⁹ have, however, used the ionic cluster in the explanation of reactions produced by alpha particles.

The possible effect of the mercury line at $184.9\text{ m}\mu$ has been neglected in this discussion. The intensity of this line should be negligible in the apparatus described.

The results reported in the present article do not conflict in any way with the findings of Dickinson and Sherrill,² but offer a possible explanation of the relatively large amount of ozone found by them. Unless it is assumed that each mercury atom passed through several complete cycles resulting in ozone formation while traversing their reaction vessel, it is necessary to find some means to explain the formation of at least seven molecules of ozone per mercury atom in their experiments. The above explanation, while somewhat artificial, would indicate that several molecules of ozone might be formed by the action of the unstable complex with excited oxygen or ozone.

Summary

1. The photochemical reaction between oxygen and mercury vapor is found to be due largely to the reaction between ozone and mercury vapor.

2. It is not possible to explain the phenomena observed by assuming that ozone is formed by both the sensitized and unsensitized reactions and that the effects are additive. It is suggested, therefore, that a complex (relatively unstable) may be formed between excited mercury and oxygen and that this complex may give ozone through collision with oxygen molecules, or perhaps a larger amount of ozone through collision with activated oxygen or ozone molecules.

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⁹ See, for example, Lind and Bardwell, *THIS JOURNAL*, **48**, 2335 (1926).

[CONTRIBUTION FROM THE BUREAU OF METALLURGICAL RESEARCH, CARNEGIE
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THE CRYSTAL STRUCTURES OF TWO INTERMETALLIC COMPOUNDS

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Introduction

The elementary constituents of alloys can be divided into three general classes:¹ pure metals and metalloids, solid solutions and intermetallic compounds. The application of x-ray methods to the study of these constituents has led to the determination of the crystal structures of the metals commonly used in alloys and has thrown considerable light on the structure of solid solutions and some of the intermetallic compounds. In order to obtain more information regarding the structure of the third class of constituents, the crystal structures of two of the intermetallic compounds formed by copper, Cu_2Mg and CuAl_2 , have been determined by x-ray methods. Cu_2Mg is one of the two compounds formed in the copper-magnesium system.^{2,3} CuAl_2 is the most important intermetallic compound formed in the copper-aluminum system^{4,5,6,7} and is likewise an important constituent in duralumin and some of the other light alloys.

Crystals of these intermetallic compounds were formed by melting together the necessary amounts of the constituent metals and slowly cooling the melt in an electric furnace. In this way a coarsely crystalline mass was obtained from which individual crystals were separated for the production of Laue and rotation photographs.

The Crystal Structure of Cu_2Mg

The size and shape of the unit cell for crystals of this compound were determined from data furnished by powder and rotation photographs taken with the K-radiation from molybdenum. The observed spacings, d , from a powder photograph are shown in the second column of Table I. Comparison with the charts of Hull and Davey⁸ shows that these spacings are among those to be expected from a face-centered cubic lattice. The indices of the reflecting planes are shown in the first column of the table,

¹ Jeffries and Archer, "The Science of Metals," McGraw-Hill Book Co., Inc., New York, 1924, p. 219.

² Sahmen, *Z. anorg. Chem.*, **57**, 1 (1908).

³ Urasow, *J. Russ. Phys.-Chem. Soc.*, **39**, 1566 (1907).

⁴ Carpenter and Edwards, *Proc. Inst. Mech. Eng.*, (London), **71**, 57 (1907).

⁵ Curry, *J. Phys. Chem.*, **11**, 425 (1907).

⁶ Gwyer, *Z. anorg. Chem.*, **57**, 113 (1908).

⁷ Stockdale, *J. Inst. Metals*, **31**, 275 (1924).

⁸ Hull and Davey, *Phys. Rev.*, **17**, 549 (1921).

and the values for the side of the unit cube computed from the observed spacing of a plane and its indices are given in the third column. The mean of these values for the side of the unit cube is 6.99 Å., which is in agreement with values of 6.98 Å. and 7.00 Å., obtained from another powder photograph and from a rotation photograph taken with one of the crystals used for producing the Laue photographs. The mean of these three values gives 6.99 Å. for the side of the unit cube. This unit cell is also in agreement with the data from the Laue photographs.

TABLE I
OBSERVED SPACINGS FROM A POWDER PHOTOGRAPH

hkl	d	a
111	4.045	7.007
220	2.473	6.995
113	2.107	6.987
222	2.019	6.995
400	1.745	6.979
133	1.604	6.992
151-333	1.345	6.990
440	1.236	6.992
135	1.184	7.008
260	1.100	6.957
226	1.055	6.997

Cubic axes, $a = 6.99$ Å.

The density of the compound was found to be 5.85 by a direct determination in a specific gravity bottle. The computed number of molecules in the unit cube is 8.00.

The Laue photographs obtained from crystals of this compound have the symmetry to be expected from the point groups T^d , O , or O^h . No first-order reflections were found from any planes save those with all indices odd; consequently only atomic arrangements based on a face-centered cubic lattice were considered.

Reference to a tabulation of the results of the theory of space groups⁹ shows that the possible atomic arrangements which must be considered are those which arise from space-groups T_d^2 and O_h^7 (or O^4). The structures which may be obtained from T_d^2 contain a variable parameter and should give second-order reflections from planes having two indices even and one odd, except for special values of the parameter. No second-order reflections were found from any such planes, although a number were in a position to produce a reflection at a favorable wave length. It is consequently concluded that the parameter must have a value close to the special values which give zero intensity of reflection for planes of this kind. With this restriction on the value of the parameter, certain of the structures

⁹ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," The Carnegie Institution of Washington, Washington, 1922.

obtained from T_d^2 can be readily eliminated, and the others can be shown to be indistinguishable from the structures obtained from O_h^7 .

Two distinct atomic arrangements may be obtained from O_h^7 (or O^4). One of these gives results which are not in agreement with the data. In the other the atoms have the following positions.

Mg: 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0; 0, 0, 0; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{3}{4}$; $\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4}$; $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$; $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$.

Cu: $\frac{1}{8}$, $\frac{3}{8}$, $\frac{7}{8}$; $\frac{7}{8}$, $\frac{1}{8}$, $\frac{3}{8}$; $\frac{3}{8}$, $\frac{7}{8}$, $\frac{1}{8}$; $\frac{3}{8}$, $\frac{5}{8}$, $\frac{3}{8}$; $\frac{1}{8}$, $\frac{5}{8}$, $\frac{1}{8}$; $\frac{1}{8}$, $\frac{1}{8}$, $\frac{5}{8}$; $\frac{5}{8}$, $\frac{1}{8}$, $\frac{5}{8}$; $\frac{5}{8}$, $\frac{5}{8}$, $\frac{7}{8}$; $\frac{7}{8}$, $\frac{3}{8}$, $\frac{1}{8}$; $\frac{1}{8}$, $\frac{7}{8}$, $\frac{3}{8}$; $\frac{3}{8}$, $\frac{1}{8}$, $\frac{7}{8}$; $\frac{5}{8}$, $\frac{3}{8}$, $\frac{3}{8}$; $\frac{7}{8}$, $\frac{5}{8}$, $\frac{7}{8}$; $\frac{7}{8}$, $\frac{7}{8}$, $\frac{5}{8}$; $\frac{5}{8}$, $\frac{7}{8}$, $\frac{7}{8}$; $\frac{3}{8}$, $\frac{3}{8}$, $\frac{5}{8}$.

This structure gives predicted intensities which are in qualitative agreement with the observed intensities as shown in Table II, which contains

TABLE II
DATA FROM A LAUE PHOTOGRAPH

$hkl(n)$	d/n	λ	I	S^2	$hkl(n)$	d/n	λ	I	S^2
133	1.60	0.37	100	27	557	0.70	0.44	10	27
112 (2)	1.42	.37	40	9	034 (2)	.70	.32	0	0
135	1.18	.41	82	27	134 (2)	.68	.46	2	9
335	1.06	.47	95	90	159	.68	.37	16	90
113 (2)	1.05	.48	125	215	377	.68	.39	15	90
155	.98	.39	37	27	359	.65	.37	5	27
023 (2)	.97	.31	0	0	234 (2)	.65	.31	0	0
123 (2)	.93	.40	8	9	125 (2)	.64	.38	2	9
355	.91	.36	57	90	179	.61	.33	4	27
137	.91	.46	62	90	559	.61	.43	3	27
157	.81	.34	37	90	035 (2)	.60	.37	1	9
012 (4)	.78	.42	67	135	379	.59	.42	8	90
357	.77	.35	11	27	122 (4)	.58	.37	11	135
124 (2)	.76	.33	0	0	579	.56	.34	5	90
233 (2)	.74	.31	3	9	013 (4)	.55	.42	13	314
139	.73	.44	25	90	779	.52	.37	1	27

data from a Laue photograph taken with the incident beam of x-rays nearly perpendicular to a (111) plane of the crystal. The first column contains hkl , the indices of the form to which the reflecting plane belongs, followed by the order of reflection, n , if this is different from unity; the second column, the spacing of the plane divided by the order of reflection; the third column the wave length of the x-rays producing the reflection; while the fourth and fifth columns contain the observed intensity, I , and the square of the amplitude factor, S . The greatest intensity of reflection is for wave lengths between 0.35 Å. and 0.40 Å. and the data have been given for these wave lengths when possible. The observed intensities are visual estimates made by comparison with a plate which had been given a series of known exposures. The structure factors have been computed on the assumption that the scattering powers of copper and aluminum atoms are proportional to their atomic numbers. The agree-

ment is probably as good as can be expected because of the approximations involved in the computation of S , and since none of the other possible structures is satisfactory, it is concluded that the proposed structure gives the atomic arrangement in crystals of Cu_2Mg .

The atoms in this crystal have the same arrangement that has been found for the metallic atoms in spinel,^{10,11} MgAl_2O_4 , and in the complex cyanides of potassium with zinc, cadmium and mercury,¹² $\text{K}_2\text{Zn}(\text{CN})_4$, $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$.

The least distance between two magnesium atoms is 3.03 Å., between two copper atoms, 2.47 Å., and between a copper and a magnesium atom, 2.90 Å. The corresponding values found by adding the radii which magnesium and copper atoms have in metallic magnesium and copper are 3.22 Å., 2.55 Å. and 2.88 Å.

The Crystal Structure of CuAl_2

The crystal structure of this compound has been the subject of two previous investigations. Owen and Preston¹³ used the powder method and concluded that one molecule of CuAl_2 is contained in a tetragonal unit cell with $a = 4.28$ Å. and $c = 2.40$ Å. Somewhat later, Jette, Phragmén and Westgren¹⁴ obtained Laue and rotation photographs from crystals of this compound and found it necessary to use a larger tetragonal unit cell which contains four molecules and has the dimensions, $a = 6.052$ Å. and $c = 4.878$ Å. The atomic arrangement was not determined in detail but was said to be body-centered with the symmetry of one of the crystal classes, V^d , D_4 , C_4^v or D_4^h .

In the present investigation, the size and shape of the unit cell were determined from rotation photographs taken with the K-radiation of molybdenum. If a rotation photograph of a tetragonal crystal rotating about a vertical axis which coincides with the c axis of the crystal is taken on a flat photograph plate perpendicular to the incident beam of x-rays, it can be shown that¹⁵

$$\frac{\lambda}{c} = \frac{V}{(V^2 + H^2 + D^2)^{1/2}} \quad (1)$$

where l is the third Miller index of the plane which produces a given spot on the photograph; λ , the wave length of the x-rays; c , the height of the unit cell; D , the distance from the crystal to the plate; and V and H the vertical and horizontal coördinates of the spot measured from the place where the incident beam of x-rays strikes the plate. Table III contains

¹⁰ Bragg, *Phil. Mag.*, 30, 305 (1915).

¹¹ Nishikawa, *Proc. Tokyo Math. Phys. Soc.*, 8, 199 (1915).

¹² Dickinson, *THIS JOURNAL*, 44, 774 (1922).

¹³ Owen and Preston, *Proc. Phys. Soc. London*, 36, 14 (1923-24).

¹⁴ Jette, Phragmén and Westgren, *J. Inst. Metals*, 31, 193 (1924).

¹⁵ Ewald, "Kristalle und Röntgenstrahlen," Julius Springer, Berlin, 1923, p. 270.

the data from a rotation photograph taken with the crystal oriented in this way. The first column contains the Miller indices, h, k, l , of the form to which the reflecting plane belongs; the second column, the values of $V(V^2 + H^2 + D^2)^{-1/2}$, computed from the observed quantities, V, H and D ; the third column, the values of the second column divided by l ; while the fourth and fifth columns contain, respectively the observed spacing, d , and the spacing computed for a tetragonal unit cell with $a = 6.04 \text{ \AA.}$ and $c = 4.86 \text{ \AA.}$ Since λ and c are constants and l is an integer, Equation (1) requires that the observed values of $V(V^2 + H^2 + D^2)^{-1/2}$ should be integral multiples of the constant λ/c . The constancy of the values in the third column of the table shows that this condition is satisfied and their mean gives 4.86 \AA. for the least value which can be assumed for c . Integral multiples of this are also possible. The data from this photograph and from a number of others taken with the crystal rotating about different crystal axes, indicate that the smallest unit cell which is possible has $a = 6.04 \text{ \AA.}$ and $c = 4.86 \text{ \AA.}$ No data were found on the rotation or the Laue photographs which would necessitate the use of a larger unit cell. These values for the dimensions agree well with those obtained by Jette, Phragmén and Westgren.

TABLE III
DATA FROM A ROTATION PHOTOGRAPH

hkl	$(V^2 + H^2 + D^2)^{1/2}$	$l(V^2 + H^2 + D^2)^{1/2}$	Observed spacing	Calcd. spacing
110	0		4.266	4.271
211	0.1468	0.1468	2.360	2.361
220	0		2.135	2.136
112	.2916	.1458	2.110	2.112
310	0		1.906	1.910
222	.2912	.1456	1.604	1.604
312	.2919	.1460	1.500	1.502
411	.1460	.1460	1.402	1.403
213	.4392	.1464	1.391	1.389
420	0		1.351	1.351
332	.2916	.1458	1.232	1.228
510	0		1.182	1.185
422	.2929	.1464	1.180	1.180
521	.1454	.1454	1.095	1.093
413	.4373	.1458	1.086	1.087
440	0		1.071	1.068
512	.2904	.1452	1.064	1.065
530	0		1.037	1.036
622	.2918	.1459	0.891	0.889

Tetragonal axes, $a = 6.04 \text{ \AA.}$; $c = 4.86 \text{ \AA.}$

The density of CuAl_2 was determined by weighing in a specific gravity bottle and was found to be 4.37. This gives 4.00 molecules in the unit cell.

The Laue photographs taken with the incident beam of x-rays perpendicular to the (001) plane have a four-fold symmetry axis and four planes of symmetry, while those taken with the incident beam perpendicular to a (100) or a (110) plane have a two-fold axis and two planes of symmetry. The atomic arrangement must consequently be obtained from some space group isomorphous with one of the point-groups V^d , C_4^v , D_4 or D_4^h , and since no reflections were observed from any planes save those for which the sum of the indices is an even number, only body-centered arrangements were considered. This restriction is in agreement with the conclusions regarding the atomic arrangement which were reached by Jette, Phragmén and Westgren.

Reference to a tabulation of the results of the theory of space groups⁹ shows that there are numerous possible body-centered arrangements with four atoms of one kind and eight of another kind in the unit cell. Many of these possibilities are readily eliminated. Careful consideration of the remaining possibilities shows that the most satisfactory agreement with the data is obtained for the atomic arrangement which places the atoms in the following positions.

Cu: 0, 0, 0; 0, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0.

Al: u , $u + \frac{1}{2}$, $\frac{1}{4}$; $\frac{1}{2} - u$, u , $\frac{1}{4}$; \bar{u} , $\frac{1}{2} - u$, $\frac{1}{4}$; $u + \frac{1}{2}$, \bar{u} , $\frac{1}{4}$; $u + \frac{1}{2}$, u , $\frac{3}{4}$; u , $\frac{1}{2} - u$, $\frac{3}{4}$; $\frac{1}{2} - u$, \bar{u} , $\frac{3}{4}$; \bar{u} , $u + \frac{1}{2}$, $\frac{3}{4}$.

This arrangement may be obtained from D_{4h}^{18} and equivalent arrangements may be obtained from several other space groups. One of the characteristic features of such an atomic arrangement is that it predicts zero intensity of reflection from all planes of the forms $(0kl)$ where k and l are both odd. No reflections from any planes of these forms were found on any of the photographs, although a considerable number of planes of this kind were in a position to produce reflections at favorable wave lengths. Furthermore, the copper atoms contribute nothing to reflections from planes of the forms (hkl) where l is odd, and h and k are one even and one odd. A large number of planes of this kind were present on the photographs and a consideration of their intensities enables the parameter, u , to be determined free from any uncertainty regarding the relative scattering powers of copper and aluminum atoms. In order to obtain satisfactory agreement with the data, u must be nearly equal to 0.158. Table IV contains the data from a Laue photograph taken with the incident beam of x-rays nearly perpendicular to a (110) plane of the crystal. The first column contains hkl , the indices of the form to which the reflecting plane belongs, followed by the order of reflection, n , if this is different from unity; the second column, the spacing of the plane divided by n ; the third column, the wave length of the x-rays producing the reflection; while the fourth and fifth columns contain the observed intensity, I , and the square of the structure factor, S . The most intense reflections are for wave lengths

TABLE IV
 DATA FROM A LAUE PHOTOGRAPH

$hkl(n)$	d/n	λ	I	S^2	$hkl(n)$	d/n	λ	I	S^2
114	1.17	0.41	100	26	581	0.64	0.44	5	37
012 (2)	1.13	.45	90	20	275	.63	.45	2	13
134	1.02	.43	130	110	147	.63	.45	3	15
451	0.93	.44	30	20	392	.62	.44	20	158
125	.91	.44	32	23	583	.60	.42	4	37
154	.85	.43	50	38	185	.59	.41	2	28
235	.84	.41	1	1	257	.59	.44	3	31
453	.82	.40	14	20	590	.59	.45	9	71
145	.81	.41	12	15	176	.59	.47	10	96
116	.80	.46	60	80	138	.58	.45	11	110
370	.79	.41	70	143	592	.57	.45	5	32
231 (2)	.79	.41	64	123	376	.57	.47	2	5
103 (2)	.78	.41	60	92	043 (2)	.55	.42	5	58
372	.75	.42	6	5	158	.54	.42	4	38
136	.75	.41	16	13	594	.53	.41	5	71
273	.74	.43	8	13	358	.52	.43	5	74
232 (2)	.69	.43	8	9	304 (2)	.52	.43	7	169
473	.68	.40	4	8	252 (2)	.51	.41	4	116
572	.67	.40	16	69	178	.49	.41	1	19
127	.67	.44	5	23	503 (2)	.48	.42	3	158
156	.67	.46	20	62	738	.48	.43	2	143
374	.66	.45	32	143					

between 0.40 Å. and 0.48 Å., and have been given in this region. The observed intensities are visual estimates made by comparison with a plate which had been given a series of graduated exposures. S^2 has been given instead of S , since the crystal is probably sufficiently imperfect to give reflections more nearly proportional to S^2 than to S . S has been computed in the usual way¹⁶ on the assumption that $u = 0.158$ and that the scattering powers of copper and aluminum atoms are proportional to their atomic numbers. The values of S^2 in the last column account quite satisfactorily for the observed intensities from planes which do not differ greatly in spacing, except that certain of the planes with l even give more intense reflections as compared to neighboring planes with l odd than is indicated by the corresponding values of S^2 . Discrepancies of this kind are to be expected, however, because of the approximations underlying the computation of S . A number of theoretical and experimental investigations have shown that the scattering power of an atom is not a constant proportional to the number of outer electrons it contains, but is a function of the glancing angle, θ , which decreases as θ increases. This decrease is more rapid for atoms with a small number of electrons than for atoms with a larger number, and the relative scattering powers of two atoms will con-

¹⁶ Wyckoff, "The Structure of Crystals," The Chemical Catalog Company, Inc., New York, 1924, p. 104.

sequently also be a function of θ . An exact evaluation of the changes which would be introduced into the calculated structure factors by this variation in scattering power cannot be made in the absence of a knowledge of the forms to be ascribed to the F curves for copper and aluminum atoms in crystals of CuAl_2 , but a qualitative estimate can readily be made and shows that the changes which would be introduced into S if the variation in scattering power were taken into account are in such a direction as to bring the calculated values of S^2 into better agreement with the observed intensities. The agreement is consequently thought to be satisfactory and since there is also good agreement with a Laue photograph which was taken with the incident beam of x-rays nearly perpendicular to the (001) plane of the crystal, it is concluded that the proposed structure gives a close approximation to the atomic arrangement in crystals of CuAl_2 . None of the other possible structures considered was found satisfactory.

The least distance between two copper atoms is 2.43 Å., between two aluminum atoms, 2.70 Å., and between a copper and aluminum atom 2.59 Å. These are somewhat less than the values 2.54 Å., 2.86 Å. and 2.70 Å. computed from the radii which copper and aluminum atoms have in metallic copper and aluminum.

Summary

The atomic arrangements in crystals of two of the intermetallic compounds formed by copper, Cu_2Mg and CuAl_2 , have been determined by x-ray methods.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 20 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE REACTION BETWEEN POTASSIUM CARBONATE AND SULFUR IN ALCOHOL SOLUTION

BY TENNEY L. DAVIS AND JULIAN W. HILL

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In his "Experiments and Notes about the Producibleness of Chymical Principles," appended to the second English edition of "The Sceptical Chymist," Oxford, 1680, Robert Boyle discusses the possibility of transmuting or changing into one another the so-called elements of the alchemists. As evidence that "a disposition to be dissoluble in this or that liquor may be acquir'd by mixture," he points¹ to the fact that, whereas neither "salt of tartar" (potassium carbonate) nor sulfur is soluble in "spirit of wine" (alcohol), "yet if this Salt and Sulphur be mixt together, spirit of Wine will in less than an hour and sometimes in less than a quarter

¹ Robert Boyle, *op. cit.*, p. 4. Concerning the several editions of "The Sceptical Chymist," see *Isis*, 8, 71 (1926).

of that time dissolve enough of this matter to be richly color'd by it, and this without the help of external heat."

We have verified Boyle's observation. A mixture of powdered sulfur with anhydrous potassium carbonate does indeed impart a yellow color to alcohol after a few hours' standing. After a longer interval the color is deeper, and after three or four days no further change is apparent. With boiling alcohol the reaction is very rapid. We have not been able to find in the literature any explanation of this behavior or of the reaction itself—and have accordingly made experiments to determine the matter.

The deep yellow liquid is not a colloidal solution for it shows no Tyndall effect. On dilution with water it gives a precipitate of finely divided sulfur, about the same amount of precipitate as is produced by adding water to a saturated solution of sulfur in alcohol. On acidification it gives hydrogen sulfide and a precipitate of sulfur—evidence that it contains potassium polysulfide. On shaking with metallic mercury it is rendered colorless and produces black mercury sulfide. If air is bubbled through the yellow liquid or brought in contact with it by shaking in a capacious flask, the liquid quickly loses its color and deposits a precipitate of sulfur and potassium thiosulfate. These reactions are the same as those of an aqueous solution of potassium polysulfide except, of course, that potassium thiosulfate does not precipitate when the aqueous solution is oxidized.

The precipitate which was produced by agitating the yellow alcohol solution with air was collected, dried and freed from sulfur by washing with carbon disulfide. The white residue was recrystallized from water, in which it was very soluble, and was analyzed for potassium by fuming down twice with sulfuric acid, igniting with ammonium carbonate, and weighing as K_2SO_4 . Found: potassium 41.08%, 41.08%; calculated for $K_2S_2O_3$, potassium 41.11%. The thiosulfate was further identified by qualitative tests with hydrochloric acid, silver nitrate, ferric chloride and stannous chloride.

When powdered sulfur is allowed to stand at laboratory temperature with a strong aqueous solution of potassium carbonate, the liquid becomes pale yellow after about two weeks and does not become deeply colored even after long standing. In boiling water the reaction is more rapid, but still much less rapid than it is in boiling alcohol. Although potassium carbonate is readily soluble in water, sulfur is almost entirely insoluble, and the greater speed of the reaction in alcohol solution is due to the fact that alcohol dissolves an appreciable quantity of both reagents and that the mass-action product of the concentration of the reagents in that solvent is greater in consequence. We have found that absolute ethyl alcohol solutions saturated at 25° contain in 100 cc. 0.1114 g. of anhydrous potassium carbonate, 0.0088 g. of anhydrous sodium carbonate and 0.03926 g. of sulfur. When sodium carbonate and sulfur are boiled together in alcohol, the reaction is slight and the solution becomes only faintly colored.

We have attempted to isolate and analyze the pure potassium polysulfide from the alcohol solution. The yellow liquid was filtered and evaporated to dryness in a stream of dry nitrogen, and the residue was freed from sulfur by washing with carbon disulfide. Sulfur was determined by dissolving dried and weighed portions of the orange-brown material in water, oxidizing with bromine water, and precipitating as barium sulfate. Among many analyses several pairs of checks were obtained, but the checks were discordant with one another. Although the yellow alcohol solution did not smell of hydrogen sulfide, it was found that the vapors from its evaporation, even when the evaporation was carried out at laboratory temperature, contained hydrogen sulfide enough to blacken lead acetate paper. Alcoholysis evidently occurred, potassium ethylate was undoubtedly present in varying amounts in the residues from the evaporations—and an attempt at fractional crystallization of the polysulfide from alcohol was abandoned as impracticable.

Summary

The reaction between potassium carbonate and sulfur in alcohol solution is essentially the same as in water solution but is very much more rapid. Alcohol dissolves an appreciable amount of both substances, while water dissolves a large amount of one and exceedingly little of the other. The solubilities of potassium carbonate, sodium carbonate and sulfur in absolute ethyl alcohol at 25° have been determined.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE UNIVERSITY OF VERMONT]

THE ODOR AND STRUCTURE OF CERTAIN CYCLIC ACETALS¹

BY R. R. READ, HUBBEL LATHROP AND H. L. CHANDLER

RECEIVED APRIL 21, 1927

PUBLISHED DECEMBER 10, 1927

Verley² isolated an oil from jasmine blossoms that had as a principal constituent the cyclic acetal of phenylethyleneglycol and formaldehyde-1-phenyldioxolane. This compound was synthesized and found to have the same jasmine-like odor. The corresponding derivatives from acetaldehyde and valeraldehyde proved to have similar odors.

Shortly afterwards Hesse and Müller³ reported that no trace of this acetal was to be found in jasmine oil and that the odor was due to two compounds of unknown nature in addition to phenylethyl acetate and a terpene alcohol ester.

¹ For the odor evaluation of the products described in this paper the writers are indebted to Burton T. Bush, Inc., of New York City, particularly to Dr. Ph. Chaleyey of that Company.

² Verley, *Compt. rend.*, **128**, 314 (1899).

³ Hesse and Müller, *Ber.*, **32**, 565 (1899).

Whether or not the odor of jasmine oil is due to dioxolane derivatives, it was of interest to determine whether compounds related to those described by Verley were odorous and, if so, how the odor was affected by variations in structure.

Accordingly acetals based on the following glycols have been prepared: 1-phenoxy-2,3-propanediol, 1-phenyl-1,2-propanediol, 1-phenyl-2,3-propanediol, 1-*m*-methylphenyl-2,3-propanediol and 1-*p*-methylphenyl-2,3-propanediol, using as the other component formaldehyde, acetaldehyde and, in one case, heptaldehyde.

The following dioxolane derivatives were prepared: (a) 1-phenoxy-methyl-, (b) 1-phenoxy-methyl-4-methyl-, (c) 1-phenoxy-methyl-4-*n*-hexyl-, (d) 1-phenyl-2-methyl-, (e) 1-phenyl-2,4-dimethyl-, (f) 1-phenyl-2-methyl-4-*n*-hexyl-, (g) 1-benzyl-4-methyl-, (h) 1-benzyl-, (i) 1-*m*-methylbenzyl-4-methyl-, (j) 1-*m*-methylbenzyl-, (k) 1-*p*-methylbenzyl-4-methyl-.

Conclusions were drawn as follows:

(a) Phenoxy-methyldioxolanes have markedly less odor than the corresponding phenyl, benzyl and methylbenzyl derivatives.

(b) Methylbenzyldioxolanes are less odorous than the benzyl derivatives.

(c) A methyl group in the 4 position increases the original odor but not its persistence.

A summary of the character of the odors of the dioxolanes listed above is: (a) not agreeable or lasting, similar to (b) but weaker; (b) slight, not agreeable, somewhat like diphenyl or cresyl oxide; (c) very weak, oily; (d) when fresh reminiscent of Rumanian petroleum ether, on standing has faint sweet-pea character; (e) similar to phenylglycol acetate but milder; (f) slight, not floral; (g) when fresh similar to phenylglycol acetate, not lasting; (h) when fresh has a chemical odor, on standing reminiscent of phenylpropionaldehyde and lilac; (i) slight, similar to (a) and (b); (j) very similar to phenylglycol acetate, not lasting; (k) very slight.

These acetals are not extremely stable, apparently regenerating aldehyde on long standing although repeated distillation does not affect the boiling range.

Experimental

References, methods of preparation, constants and other data on the glycols used are given in the following table.

Preparation of Dioxolanes.—These were all prepared in the same way⁴ by heating equal molal fractions of the glycol and aldehyde on a steam-bath under a reflux condenser with stirring for six hours. Five drops of 40% sulfuric acid was used as a catalyst. An excess of solid sodium carbonate was added, the oil taken up in ether, washed once with dilute carbonate solution, twice with water and then dried over sodium sulfate. After the removal of the ether the product was vacuum distilled.

⁴ Fischer and Giebe, *Ber.*, 30, 3053 (1897).

TABLE I
 DATA ON GLYCOLS USED

Name	Prepared from	B. p., °C.	d_4^{20}	Formula	Calcd. C	Calcd. H	Found C	Found H
Phenyglycerin ether ^a	176 (16 mm.)
1-Phenyl-1,2-propanediol ^b
1-Phenyl-2,3-propanediol ^c	Chlorohydrin ^d	160-163 (13 mm.)	1.115	C ₉ H ₁₀ O ₂	71.1	7.9	70.9	7.7
1- <i>o</i> -Methylphenyl-2,3-propanediol	Chlorohydrin ^e
1- <i>m</i> -Methylphenyl-2,3-propanediol ^f	Chlorohydrin ^g	165-166 (10 mm.)	1.090	C ₁₀ H ₁₄ O ₂	72.3	8.4	72.3	8.3
1- <i>p</i> -Methylphenyl-2,3-propanediol	Chlorohydrin ^h	170-172 (13 mm.)	1.074	C ₁₀ H ₁₄ O ₂	72.3	8.4	71.8	8.5

^a M. p. (from ether) 63°. Fourneau [*J. Pharm. Chem.*, [7], 1, 55 (1910); *C. A.*, 4, 3070 (1910)] gives b. p. 200° (22 mm.); m. p. 69°.

^b Zincke and Zahn, *Ber.*, 43, 849 (1900). Both alpha and beta forms. The crude dibromide is remarkably irritant on the eyes.

^c By the method of Brooks and Humphrey, *J. Ind. Eng. Chem.*, 9, 750 (1917); a viscous oil of faint, agreeable odor.

^d Fourneau and Tiffeneau, *Bull. soc. chim.*, [4], 1, 1227 (1907); *C. A.*, 2, 1273 (1908), prepared the chlorohydrin by the action of phenylmagnesium bromide on epichlorohydrin (yield, 33%), 1-chloro-3-bromo-2-propanol also being formed in 30% yield; b. p. 88-90° (20 mm.), $d_4^{20} = 1.726$ [*Ann. Suppl.*, 1, 225 (1861)].

^e Prepared according to method of ref. *d*; ratio of chlorohydrin to chlorobromopropanol, 1:9; b. p. 144-146° (20 mm.), $d_4^{20} = 1.150$.

^f Viscous liquid with faint, agreeable odor.

^g Prepared by method of ref. *d* (yield, 30%); ratio to chlorobromopropanol, 1:1; b. p. 135-150° (11 mm.).

^h Prepared by method of ref. *d*; products in same ratio as in ref. *e*.

With the hope that acetals might be formed when the corresponding oxide and aldehyde were treated with sulfuric acid, as in the case of the mixed glycol and aldehyde, benzyloxyethylene oxide was prepared from 1-phenol-3-chloro-2-propanol added to an

 TABLE II
 CONSTANTS AND DATA ON DIOXOLANES

Dioxolane	B. p., °C.	M. p., °C.	d_4^{20}	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
(a) 1-Phenoxyethyl	138-139 (11 mm.)	40-43	...	C ₁₀ H ₁₂ O ₂	66.6	6.7	66.2	6.7
(b) 1-Phenoxyethyl-4-methyl	152-154 (11 mm.)	24	...	C ₁₁ H ₁₄ O ₂	68.0	7.2	68.2	7.1
(c) 1-Phenoxyethyl-4- <i>n</i> -hexyl	201-203 (12 mm.)	C ₁₈ H ₂₄ O ₂	72.7	9.1	72.6	9.1
(d) ^a 1-Phenyl-2-methyl	104-105 (11 mm.)	C ₁₀ H ₁₂ O ₂	73.2	7.3	No analysis	
(d) ^b 1-Phenyl-2-methyl	105-107 (12 mm.)	C ₁₀ H ₁₂ O ₂	73.2	7.3	73.3	7.6
(e) 1-Phenyl-2,4-dimethyl	116-118 (19 mm.)	...	1.032	C ₁₁ H ₁₄ O ₂	74.1	7.9	74.2	7.7
(f) 1-Benzyl-4-methyl	120-124 (16 mm.)	...	1.092	C ₁₁ H ₁₄ O ₂	74.1	7.9	72.8	7.5
(g) 1-Benzyl	125-128 (16 mm.)	...	1.098	C ₉ H ₁₀ O ₂	73.2	7.3	71.0	6.8
(h) 1- <i>m</i> -Methylbenzyl-4-methyl	123-125 (13 mm.)	...	1.028	C ₁₂ H ₁₆ O ₂	75.0	8.3	74.6	8.5
(i) 1- <i>m</i> -Methylbenzyl	128-130 (15 mm.)	...	1.032	C ₁₁ H ₁₄ O ₂	74.1	7.9	73.1	7.8
(j) 1- <i>p</i> -Methylbenzyl-4-methyl	135-142 (17 mm.)	...	1.032	C ₁₂ H ₁₆ O ₂	75.0	8.3	73.5	8.3

^a From the α -glycol.

^b From the β -glycol.

equal molal quantity of trimethylene oxide with 5 drops of 40% sulfuric acid and heated for six hours on the steam-bath. The benzylethylene oxide was recovered unchanged. This is in accordance with the results obtained by Wurtz with ethylene oxide and acetaldehyde.⁵

Summary

1. Few of the dioxolanes based on phenyl-, methylphenyl- and phenoxy-propanediol have a marked agreeable odor.
2. None of the compounds has a jasmine-like odor.

BURLINGTON, VERMONT

[CONTRIBUTION FROM THE MEDICAL RESEARCH DIVISION, CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

CHLORINATION OF β,β -DICHLORO-ETHYL SULFIDE. I¹

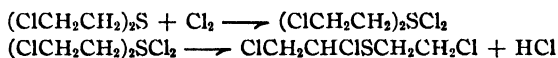
BY W. E. LAWSON AND T. P. DAWSON

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The only feasible methods for the destruction of Mustard Gas, or β,β -dichloro-ethyl sulfide, involve the use of chlorine. Small amounts in the laboratory may be oxidized with nitric acid to the sulfoxide, which is non-vesicant, that is, does not cause blistering of the skin, and under certain conditions clothing may be demustardized with live steam, but these are practically the only instances of other means for its destruction.

The ease and rapidity with which β,β -dichloro-ethyl sulfide is chlorinated suggests a preliminary addition of the chlorine followed by a molecular rearrangement involving substitution of one atom of chlorine and elimination of one molecule of hydrogen chloride² according to the equations



Certain facts that give support to this view have already been published. The sulfide is promptly oxidized to the sulfoxide by nitric acid;³ it reacts with chloramine-1 to form an addition product, $(\text{ClCH}_2\text{CH}_2)_2\text{S} = \text{NSO}_2\text{-C}_6\text{H}_4\text{CH}_3$;⁴ and it adds bromine to form a dibromide and perbromide.⁵

One paper on the chlorination of β,β -dichloro-ethyl sulfide has appeared, besides a number of chemical warfare studies. Mann and Pope⁶ chlorinated the compound to different stages with gaseous chlorine and

⁵ Wurtz, *Ann.*, **120**, 328 (1861).

¹ Published by permission of the Chief of the Chemical Warfare Service.

² It is with pleasure that we acknowledge that this suggestion was first made by Professor E. Emmet Reid of Johns Hopkins University in a discussion with one of us on the chlorination of Mustard Gas.

³ Helfrich and Reid, *THIS JOURNAL*, **42**, 1208 (1920).

⁴ Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

⁵ Gibson and Pope, *ibid.*, **117**, 271 (1920).

⁶ Mann and Pope, *J. Chem. Soc.*, **121**, 594 (1922).

isolated three compounds which they termed α,β,β' -trichlorodiethyl sulfide, $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide and $\alpha,\alpha,\beta,\beta,\beta,\beta'$ -hexachlorodiethyl sulfide. McCrumb and Reeves⁷ found that more than the theoretical quantity of hydrogen chloride was evolved on chlorination, and isolated a chloro-ethylchlorovinyl sulfide, without, however, determining the position of the chlorine atoms. Our own experience leads us to believe that it was a mixture of two isomeric compounds. Pfanstiel and Peakes⁸ also noted the evolution of hydrogen chloride in more than the theoretical amount on chlorinating the sulfide.

Our study of the chlorination of β,β -dichloro-ethyl sulfide was divided into three parts: (1) isolation of the intermediate addition product in chlorination; (2) preparation of the lower chlorinated derivatives; (3) tabulation of the different compounds theoretically possible in chlorination.

Isolation of Intermediate Addition Product

On treating a solution of β,β -dichloro-ethyl sulfide in carbon tetrachloride with chlorine at a temperature of -5 to 0° , the intermediate addition product in the process of chlorination, β,β -dichloro-ethyl sulfonium chloride, $(\text{ClCH}_2\text{CH}_2)_2\text{SCl}_2$, crystallizes from solution in white needles. The chlorine may be added directly or as a solution in carbon tetrachloride. No hydrogen chloride is liberated during this treatment. The compound is unstable at room temperature. It decomposes simultaneously in two ways, forming dichloro-ethyl sulfoxide and trichlorodiethyl sulfide, the main reaction being the formation of the latter. Solution in 95% alcohol, however, yields chiefly the sulfoxide.

Preparation of Chlorinated Sulfides

It was considered that the isolation and decomposition of β,β -dichlorodiethyl sulfonium chloride would give a very pure α,β,β' -trichlorodiethyl sulfide, one probably less contaminated by other chlorinated derivatives than the compound described as such by Mann and Pope.⁶ On distillation of this relatively pure trichlorodiethyl sulfide, great quantities of hydrogen chloride were evolved and no definite boiling point was observed. After ten distillations, two distinct fractions were obtained boiling at 73.5 – 74.5° (4 mm.) and 69.5 – 70.5° (4 mm.), respectively. Analysis showed both to have the same empirical formula, corresponding to chloro-ethylchlorovinyl sulfide. Both compounds were oxidized by dilute nitric acid to form β -chloro-ethane sulfonic acid, from which ammonium β -chloro-ethane sulfonate was obtained in small needles melting at 200° . This proved the presence of a β -chloro-ethyl group in each of the above compounds and left only the position of the chlorine on the vinyl group

⁷ McCrumb and Reeves, Chemical Warfare Report.

⁸ Pfanstiel and Peakes, Chemical Warfare Report.

in doubt. The higher-boiling compound had a sweet odor; the lower-boiling isomer had the penetrating odor of α,α -dichloro-ethyl sulfide, though the odor was not as strong. The α -chlorovinyl derivative should have a lower boiling point than the corresponding β -chlorovinyl compound. Both compounds were treated with the sodium salt of β -naphthol; the β -chloro-ethyl- β -chlorovinyl sulfide reacted with two moles, while the β -chloro-ethyl- α -chlorovinyl sulfide reacted with but one.

This would seem to complete the proof of structure, but as the proof was inferential rather than direct, the preparation and decomposition of α -bromo- β,β' -dichlorodiethyl sulfide was carried out following the method described for its chlorine analog. Decomposition during distillation was very great, but there was finally obtained a compound free from bromine having a boiling point of $77-77.5^\circ$ (4 mm.), as compared with $73.5-74.5^\circ$ (4 mm.) for the same compound in a slightly purer state made by chlorination instead of bromination. The only possible formula for this compound is β -chloro-ethyl- β -chlorovinyl sulfide, which is in accord with the inferential proof already given.

Compounds Theoretically Obtainable by Chlorination of Dichloro-ethyl Sulfide

The instability of α,β,β' -trichlorodiethyl sulfide and its decomposition on distillation to give the two isomers, β -chloro-ethyl- β -chlorovinyl and β -chloro-ethyl- α -chlorovinyl sulfides, affords an explanation for the failure of Mann and Pope⁶ to isolate pentachlorodiethyl sulfide. They considered their products to have been α,β,β' -trichlorodiethyl sulfide, analyzing 2.6% hydrogen with a theoretical value of 3.6; $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide, analyzing 1.8% hydrogen with a theoretical value of 2.6; and $\alpha,\alpha,\beta,\beta,\beta,\beta'$ -hexachlorodiethyl sulfide, analyzing 1.3% hydrogen with a theoretical value of 1.4.

We have found that α,β,β' -trichlorodiethyl sulfide is so unstable that it is absolutely impossible to isolate it by distillation at pressures as low as 3.5 mm. of mercury. The compound isolated by Mann and Pope could not, therefore, have been the trichlorodiethyl sulfide. If, however, we postulate the splitting out of hydrogen chloride from tetrachlorodiethyl sulfide to give a chloro-ethyldichlorovinyl sulfide, and if we explain similarly the decomposition of pentachlorodiethyl sulfide to give chloro-ethyltrichlorovinyl sulfide, there is afforded an explanation for the low hydrogen values obtained by them in analyzing their tri- and tetrachlorinated derivatives, and also for their inability to isolate the pentachloro derivative.

By assuming the instability of the chlorinated ethyl group after chlorination of β,β -dichloro-ethyl sulfide, the following list of compounds is theoretically possible.

TABLE I
CHLORINATION OF DICHLORO-ETHYL SULFIDE (1)

Initial comp., no.	Treatment	Compound formed		See note	B. p., °C. (corr.) 4 mm. pressure
		No.	Formula		
I	Cl ₂ by subst.	II	ClCH ₂ CHClSCH ₂ CH ₂ Cl	(1)	Unstable
II	By vac. dist.	III	ClCH:CHSCH ₂ CH ₂ Cl	(1)	73.5-74.5
		IV	CH ₂ :CCISCH ₂ CH ₂ Cl	(1)	69.5-70.5
III	Cl ₂ by add.	V	Cl ₂ CHCHClSCH ₂ CH ₂ Cl	(3)	118.5-119/3.5
IV	Cl ₂ by add.	VI	ClCH ₂ CCl ₂ SCH ₂ CH ₂ Cl	(4)	Unstable
I	2Cl ₂ by subst.	VI			
V	By vac. dist.	VII	ClCH:CCISCH ₂ CH ₂ Cl	(2)	79.5-80.5
		VIII	Cl ₂ C:CHSCH ₂ CH ₂ Cl	(3)	90-91/3
VI	By vac. dist.	VII			
VII	Cl ₂ by add.	IX	Cl ₂ CHCCl ₂ SCH ₂ CH ₂ Cl	(3)	Unstable
VIII	Cl ₂ by add.	X	Cl ₂ CCHClSCH ₂ CH ₂ Cl	(4)	Unstable
I	3Cl ₂ by subst.	IX			
IX, X	By vac. dist.	XI	Cl ₂ C:CCISCH ₂ CH ₂ Cl	(2)	98.0-98.5
XI	Cl ₂ by add.	XII	Cl ₃ CCCl ₂ SCH ₂ CH ₂ Cl	(2)	131-132
I	4Cl ₂ by subst.	XII			

(1) Prepared in this paper.

(2) Prepared by Mann and Pope.

(3) Prepared but will be published in subsequent paper.

(4) Not prepared.

Both of the chloro-ethyl chlorovinyl compounds are irritating and slightly vesicant, but by no means comparable to their parent compound, β,β -dichloro-ethyl sulfide. The higher chlorinated derivatives, saturated or unsaturated, are non-vesicant. This is also in accord with the findings of Mann and Pope.

Experimental Part

Preparation of β,β -Dichloro-ethyl Sulfonium Chloride

A sample of β,β -dichloro-ethyl sulfide weighing 15.98 g. was diluted with 50 cc. of pure, dry carbon tetrachloride in a 500cc. Pyrex boiling flask whose paraffined stopper bore a stirrer, thermometer, dropping funnel, and an exit tube filled with calcium chloride. A solution of chlorine in dry carbon tetrachloride containing 7.13 g. of chlorine was also prepared. Flasks and solutions were chilled to -5° , after which the chlorine solution was slowly added, the temperature being maintained at -5 to 0° . A white precipitate appeared very soon after the addition of the chlorine solution was begun and increased in amount as more chlorine was added. The precipitate was filtered off on a Büchner funnel, washed with cold carbon tetrachloride, and transferred to a small Erlenmeyer flask. In about three minutes the mass began to liquefy; the reaction increased with rapidity and was complete in about two more minutes, leaving a colorless liquid. Hydrogen chloride was evolved in great quantity during the decomposition but was not evident before. The reaction was slightly endothermic. This decomposition does not take place when a thin layer is placed in a desiccator or spread out on filter paper in the open air. Instead, the chloride was found to be slowly converted to the sulfoxide. This suggests that the chlorination reaction may be catalyzed by hydrogen chloride. Alcohol increases sulfoxide formation, for pure sulfoxide was obtained by dissolving the sulfonium chloride in 95% alcohol.

Samples of the solid addition product were weighed into dry tared flasks and connected with bubblers containing sodium hydroxide solution. Dry air was used to sweep the liberated hydrogen chloride into the standard alkali solution. Only 64 to 73% of the theoretical amount of hydrogen chloride was collected, showing that considerable decomposition had taken place during the isolation and weighing of the material. This was confirmed by immersing the addition product in sodium hydroxide solution. After standing for ten days so as to insure complete hydrolysis of the chlorine, but 62.5% was accounted for.

Preparation of Chlorinated Sulfides

A modified Dufton column⁹ of Pyrex glass was constructed, 57 cm. in length from constriction to side outlet and with an internal diameter of 18 mm. The column was well lagged with asbestos paper and provided with a nichrome wire heating element. The distilling flask was immersed in a Wood's metal bath.

β,β -Dichloro-ethyl sulfide was chlorinated in four lots of 100 g. each diluted with 300 cc. of dry carbon tetrachloride. Chlorine gas was passed in at about 35 cc. per minute, the solution being stirred vigorously throughout the period of addition and maintained at a temperature below 35°. The reaction products from the four runs were combined, freed from carbon tetrachloride by distilling under reduced pressure, then distilled twice at 5 to 6 mm. pressure; yield, 358 g.

This product was then distilled through the Dufton column at the rate of one drop every three to four seconds; yield, 284 g. After seven more distillations through the column, collecting separate fractions every two or three degrees, the isomers were finally separated in a comparatively pure state: β -chloro-ethyl- β -chlorovinyl sulfide, b. p. 73.5–74.5° (4 mm.), yield 130 g.; β -chloro-ethyl- α -chlorovinyl sulfide, b. p. 69.5–70.5° (4 mm.), yield 60 g.

The greater stability of the β -halogen, indicated above by the respective yields of the two isomers, was also shown by an analysis of the exit gases from the decomposition of α -bromo- β,β' -dichlorodiethyl sulfide. This showed 74% of hydrogen bromide and 26% of hydrogen chloride.

The following new compounds were prepared and identified in connection with this study.

β,β -Dichloro-ethylsulfonium Chloride.—Formed by the addition of chlorine to β,β -dichloro-ethyl sulfide at about 0°. Colorless needles; insoluble in carbon tetrachloride; decomposes at room temperature to form α,β,β' -trichlorodiethyl sulfide and hydrogen chloride, the hydrogen chloride apparently acting as a catalyst to speed up the reaction. In the presence of water or water vapor another reaction takes place, giving β,β -dichloro-ethyl sulfoxide and hydrogen chloride.

α,β,β' -Trichlorodiethyl Sulfide.—Colorless liquid formed by the decomposition of β,β -dichloro-ethyl sulfonium chloride. It decomposes slowly at room temperature with evolution of hydrogen chloride and cannot be distilled at a pressure as low as 3.5 mm.; $d_4^{20} = 1.4038$; $n_D^{22.5} = 1.5309$.

⁹ Dufton, *J. Soc. Chem. Ind.*, **38**, 45 (1919).

β -Chloro-ethyl- β -chlorovinyl Sulfide.—Colorless oil obtained by repeated fractionation of the distillation product of α,β,β' -trichlorodiethyl sulfide; b. p. 73.5–74.5° (4 mm.); $d_4^{20} = 1.3280$, $n_D^{22.5} = 1.5483$.

Anal. Calcd., S, 20.42. Found: 20.03, 19.80. Calcd., Cl, 45.16. Found: 46.11, 46.27.

It was also obtained by repeated distillation of α -bromo- β,β' -dichlorodiethyl sulfide, but the purification was more difficult; b. p. 77.0–77.7° (4 mm.).

Anal. Calcd., S, 20.42. Found: 20.46, 20.35. Calcd., Cl, 45.16. Found: 43.87, 43.91; Br, none.

β -Chloro-ethyl- α -chlorovinyl Sulfide.—Colorless liquid obtained with the β -chlorovinyl compound by repeated fractionation of the distillation product of α,β,β' -trichlorodiethyl sulfide, b. p. 69.5–70.5° (4 mm.); $d_4^{20} = 1.3193$; $n_D^{22.5} = 1.550$. It is produced in only about one-half the quantity of its β -chlorovinyl isomer.

Anal. Calcd., S, 20.42. Found: 20.19, 20.27. Calcd., Cl, 45.16. Found: 45.10, 44.99.

α -Bromo- β,β' -dichlorodiethyl Sulfide.—Yellow oil obtained from β,β -dichloro-ethyl sulfonium bromide by allowing it to stand for several days in a flask. When kept in a desiccator this decomposition was found not to take place. The compound is unstable even at room temperature and shortly decomposes into a black, tarry mass. When distilled it decomposes to give a variety of products of which only β -chloro-ethyl- β -chlorovinyl sulfide has been isolated.

Bis(β -naphthoxy)-ethylvinyl Sulfide.—Crystals, tiny, diamond-shaped plates, obtained by refluxing a solution of β -chloro-ethyl- β -chlorovinyl sulfide in absolute alcohol with sodium naphthionate for twelve hours on the water-bath and recrystallizing the product from hot absolute alcohol; m. p. 129.5° (corr.).

Anal. Calcd., S, 9.40. Found: 8.51. Cl, none. Found: none by qualitative test.

β -Naphthoxy-ethyl- α -chlorovinyl Sulfide.—Secured by treatment of β -chloro-ethyl- α -chlorovinyl sulfide with sodium naphthionate in the same manner as described above. The oil at first obtained gives crystals on treatment with petroleum ether; m. p. 56–57° (corr.).

Anal. Calcd., S, 12.90. Cl present by qualitative test (not enough sample for both Cl and S analyses).

Summary

1. It has been shown that β,β -dichloro-ethyl sulfonium chloride is the intermediate addition product in the chlorination of β,β -dichloro-ethyl sulfide and that it decomposes to give α,β,β' -trichlorodiethyl sulfide.

2. Distillation of α,β,β' -trichlorodiethyl sulfide gives two isomeric vinyl compounds, β -chloro-ethyl- β -chlorovinyl and β -chloro-ethyl- α -chlorovinyl sulfide. These have been isolated and proof of their structure has been obtained.

3. On the basis of the splitting out of hydrogen chloride to give the corresponding vinyl compound, there has been formulated a theory to account for the absence of pentachlorodiethyl sulfide from the chlorination product of β,β -dichloro-ethyl sulfide obtained by Mann and Pope. In accordance with this theory, the two lower chlorinated products obtained by them were chloro-ethylchlorovinyl sulfides. Their analyses check such formulas very closely.

4. A number of the chlorinated and brominated products from β,β -dichloro-ethyl sulfide together with some of their derivatives have been prepared.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE MEDICAL RESEARCH DIVISION, CHEMICAL WARFARE SERVICE,
EDGEMOOD ARSENAL]

CHLORINATION OF β,β -DICHLORO-ETHYL SULFIDE. II¹

BY T. P. DAWSON AND W. F. LAWSON

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In a previous article² there was given a table showing the total number of compounds theoretically possible on treatment of β,β -dichloro-ethyl sulfide with chlorine. The hypothesis on which this table was based is, in brief, that β,β -dichloro-ethyl sulfide will react with one, two, three, or four molecules of chlorine to give the corresponding tri-, tetra-, penta-, and hexachloro derivatives, in each of which only one ethyl group takes part in the reaction. On distillation of the three lower chlorinated compounds one molecule of hydrogen chloride splits out to give a chloro-ethyl mono-, di-, or tri-chlorovinyl sulfide. The chlorine may split out from either the alpha or beta position. The hexachloro product, having no hydrogen in the chlorinated ethyl group, distills unchanged.

This article describes the preparation of practically all of the compounds theoretically possible which were not given in the first paper, that is, the tetra-, penta-, and hexachlorodiethyl sulfides and the tri- and tetrachloro-ethylvinyl sulfides. None of the compounds is vesicant, that is, has skin-blistering properties.

Tetrachlorodiethyl Sulfide and its Decomposition Products

According to the above hypothesis, two tetrachloro isomers are possible, with the chlorine in the $\alpha,\alpha,\beta,\beta'$ - and $\alpha,\beta,\beta,\beta'$ -positions, respectively. They may be made by the addition of one molecule of chlorine to the respective unsaturated dichloro derivative. The $\alpha,\alpha,\beta,\beta'$ -isomer may also be prepared by treatment of β,β -dichloro-ethyl sulfide with two equivalents of chlorine, both chlorine atoms substituting in the alpha position. This isomer is so unstable that when distilled it breaks down completely into β -chloro-ethyl- α,β -dichlorovinyl sulfide. No isomer of this vinyl compound is possible since hydrogen atoms are present only on the beta carbon of the saturated parent compound. A high yield is secured.

On treating a mixture of the two chloro-ethylchlorovinyl isomers with

¹ Published by permission of the Chief of the Chemical Warfare Service.

² Lawson and Dawson, *THIS JOURNAL*, 49, 3119 (1927).

one molar equivalent of chlorine and distilling the reaction product, there is obtained a good yield of β -chloro-ethyl- α,β -dichlorovinyl sulfide (from β -chloro-ethyl- α -chlorovinyl sulfide by addition of chlorine to form the unstable $\alpha,\alpha,\beta,\beta'$ -tetrachlorodiethyl sulfide) and, in addition, a comparatively stable saturated tetrachloro derivative. This must have originated from β -chloro-ethyl- β -chlorovinyl sulfide and has, therefore, the structure $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide. When heated under reflux instead of distilled, this compound decomposes into an unsaturated trichloro derivative, boiling at $90-91^\circ$ (3.5 mm.) or 10° above its β -chloro-ethyl- α,β -dichlorovinyl isomer. Theoretically, $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide should give two isomeric unsaturated trichloro compounds, but only the one was isolated, and this must have had the structure β -chloro-ethyl β,β -dichlorovinyl sulfide. Whether the other was formed in small amounts or was not formed at all we were not able to determine with the small amount of tetrachlorodiethyl sulfide on hand.

Pentachlorodiethyl Sulfide and its Decomposition Product

Mann and Pope³ were unable to isolate a pentachlorodiethyl sulfide by chlorination of β,β -dichloro-ethyl sulfide and distillation of the reaction product, a fact which is in agreement with its postulated instability. Two pentachloro derivatives are theoretically possible, $\alpha,\alpha,\beta,\beta,\beta'$ - and $\alpha,\beta,\beta,\beta,\beta'$ -. We obtained the former by adding exactly one molar equivalent of chlorine to pure β -chloro-ethyl- α,β -dichlorovinyl sulfide in carbon tetrachloride solution. The compound was isolated without distillation. Analysis of the product showed a pentachloro derivative. Because of the small amount of β -chloro-ethyl- β,β -dichlorovinyl sulfide on hand no effort was made to prepare the isomeric pentachloro sulfide.

When this addition product of chloro-ethyldichlorovinyl sulfide and chlorine was distilled, there was secured an unsaturated tetrachloro derivative in excellent yield, with no trace of a pentachloro compound. Pentachlorodiethyl sulfide decomposes slowly even at room temperature and on distillation gives an almost quantitative yield of β -chloro-ethyl- α,β,β -trichlorovinyl sulfide. No isomer of this compound is possible.

Hexachlorodiethyl Sulfide

When all the hydrogen atoms on the one ethyl group have been substituted by chlorine, formation of vinyl compounds becomes impossible and a stable saturated compound is first encountered. Mann and Pope³ isolated $\alpha,\alpha,\beta,\beta,\beta,\beta'$ -hexachlorodiethyl sulfide by chlorinating β,β -dichloro-ethyl sulfide. They were unable to secure any chlorination on the second ethyl group. Their findings have been confirmed by us.

³ Mann and Pope, *J. Chem. Soc.*, 121, 594 (1922).

Experimental Part

The same procedure was employed in the addition of chlorine to the higher chlorinated derivatives as was described in the previous paper on the chlorination of β,β -dichloro-ethyl sulfide. Chlorine was passed through an accurately calibrated flowmeter into a solution in carbon tetrachloride of the compound to be chlorinated. As an additional precaution beyond those previously observed, the exit tube from the reaction flask was immersed in potassium iodide solution and the escaping chlorine was titrated. This was found negligible in the case of reactions by which tetrachloro derivatives are formed. On completion of the reaction the solvent was distilled off and the residue was vacuum distilled twice from an ordinary distilling flask. The distillate was then fractionated with the aid of the modified Dufton column⁴ until constant-boiling products were obtained. Boiling points were obtained by making a final distillation from an ordinary distilling flask so as to avoid any danger of superheating the vapor in the electrically heated Dufton column. Isolation of comparatively pure products was obtained much more readily than expected in view of the difficulty in separating the two chloro-ethylchlorovinyl isomers previously described. Analyses for both sulfur and chlorine were carried out by the Parr bomb method.⁵

$\alpha,\beta,\beta,\beta'$ -Tetrachlorodiethyl Sulfide.—A solution of a 100g. mixture of the two isomeric chloro-ethylchlorovinyl sulfides in 200 cc. of dry carbon tetrachloride was treated with one molar equivalent of chlorine (45.2 g.), the chlorine being added at the rate of 35.2 cc. per minute. After four distillations from an ordinary distilling flask and eight through the Dufton column, a fraction boiling at 118.5–119° (3 mm.) was obtained; yield, 17 g.

Anal. Calcd. for $C_4H_6SCl_4$: Cl, 62.22. Found: 61.99, 62.53.

Accompanying this fraction was another which had a boiling point and chlorine content closely approaching those for β -chloro-ethyl- α,β -dichlorovinyl sulfide.

$\alpha,\alpha,\beta,\beta'$ -Tetrachlorodiethyl Sulfide.—This compound is too unstable to be isolated by distillation. On distillation its decomposition product, β -chloro-ethyl- α,β -dichlorovinyl sulfide, is always obtained.

β -Chloro-ethyl- α,β -dichlorovinyl Sulfide.—A sample of 100 g. of β,β -dichloro-ethyl sulfide dissolved in 200 cc. of dry carbon tetrachloride was treated with 89.25 g. of chlorine (2 molar equivalents) through a period of fourteen and one-half hours. After two distillations from an ordinary distilling flask and one through the Dufton column, a large fraction boiling at 79.7–80.5° (4 mm.) was secured; yield, 63 g.

A boiling point of 108.5–109° (15 mm.) was observed. Mann and Pope give 106.5–108° (15 mm.) for the compound they termed α,β,β' -trichlorodiethyl sulfide.

Anal. Calcd. for $C_4H_5SCl_3$: Cl, 55.55; S, 16.74. Found: Cl, 55.59, 55.51; S, 16.48, 16.63.

The compound was also formed by the addition of one molar equivalent of chlorine to a mixture of the two isomeric chloro-ethylchlorovinyl sulfides; b. p. 80–81° (4 mm.).

⁴ Dufton, *J. Soc. Chem. Ind.*, **38**, 45 (1919).

⁵ All analyses were made by the Analytical Department, Chemical Division.

After oxidation with dilute nitric acid, ammonium β -chloro-ethane sulfonate was isolated and identified, following the procedure described in the previous paper.

β -Chloro-ethyl- β,β -dichlorovinyl Sulfide.—A sample of 14 g. of $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide was refluxed in an oil-bath at 150–160° for fourteen hours. On distillation there was readily obtained an unsaturated trichloro derivative boiling at 90–91° (3.5 mm.) as compared with 79.5–80.5° (4 mm.) for β -chloro-ethyl- α,β -dichlorovinyl sulfide. The only unsaturated isomer for the latter compound would have the structure corresponding to the formula given above, and such a compound would be expected from its synthesis; yield, 9 g.

Anal. Calcd. for $C_4H_5SCl_3$: Cl, 55.55; S, 16.74. Found: Cl, 56.01, 56.30; S, 16.12, 15.32.

β -Chloro-ethyl- α,β,β -trichlorovinyl Sulfide.—To a sample of 100 g. of β -chloro-ethyl- α,β -dichlorovinyl sulfide dissolved in 200 cc. of dry carbon tetrachloride was added one molar equivalent of chlorine (37.05 g.), at a reaction temperature of 50–60°. No hydrogen chloride was evolved during the entire run and all but 0.035 g. of the chlorine was absorbed. After but two distillations, once from an ordinary distilling flask and once through the Dufton column, a large fraction boiling at 97–98° (4 mm.) was secured; yield, 68 g. A boiling point of 123.5–124.5° (15 mm.) was observed. Mann and Pope give 123–125° (15 mm.) for the compound they termed $\alpha,\beta,\beta,\beta'$ -tetrachlorodiethyl sulfide.

Anal. Calcd. for $C_4H_4SCl_4$: Cl, 62.77; S, 14.19. Found: Cl, 62.68, 62.54; S, 13.84, 14.06.

Since no hydrogen chloride came off during the chlorination, a pentachlorodiethyl sulfide must have been formed and subsequently decomposed during distillation into the unsaturated tetrachloro compound.

$\alpha,\alpha,\beta,\beta,\beta'$ -Pentachlorodiethyl Sulfide.—A sample of pure β -chloro-ethyl- α,β -dichlorovinyl sulfide weighing 13 g. was dissolved in 100 cc. of carbon tetrachloride and 5.0 g. of chlorine (equivalent to one gram mole) was added. Absorption was almost complete. No hydrogen chloride was evolved. The bath in which the reaction flask was immersed was maintained at 60 to 70°. After the completion of the reaction, the solvent was removed under reduced pressure and the oil washed three times with a dilute aqueous solution of sodium bisulfite, then three times with a dilute solution of sodium carbonate, and finally shaken with water. The oil was extracted with ether, the ether solution dried with fused sodium sulfate, and the ether distilled off under vacuum. During this last operation some hydrogen chloride was evolved.

Anal. Calcd. for $C_4H_3SCl_5$: Cl, 67.55; S, 12.22. Found: Cl, 66.2, 67.3; S, 12.56, 12.55.

This compound breaks down completely on distillation to give the unsaturated β -chloro-ethyl- α,β,β -trichlorovinyl sulfide.

$\alpha,\alpha,\beta,\beta,\beta,\beta'$ -Hexachlorodiethyl Sulfide.—A sample of completely chlorinated β,β -dichloro-ethyl sulfide⁶ which had been made by treatment with an excess of chlorine at room temperature was separated into three main fractions by distillation through the Dufton column: (1) a mixture of low-boiling chlorinated hydrocarbons; (2) the unsaturated tetrachloro compound, β -chloro-ethyl- α,β,β -trichlorovinyl sulfide; (3) hexachlorodiethyl sulfide.

The hydrocarbons were not pure, analyzing 0.66% of sulfur and 81.26% of chlorine. The tetrachloro compound had the same boiling point as the one obtained by adding one gram mole equivalent of chlorine to β -chloro-ethyl- α,β -dichlorovinyl sulfide and

⁶ Furnished us through the courtesy of Dr. J. S. Reichert, Anti-Gas Department, Chemical Division.

distilling. It analyzed 62.52, 62.08% of chlorine and 13.39, 13.51% of sulfur, as compared with theoretical values of 62.77 and 14.19, respectively. $\alpha, \alpha, \beta, \beta, \beta, \beta'$ -Hexachlorodiethyl sulfide boils at 131–132° (4.5 mm.) or 159.5–160° (15 mm.). Mann and Pope³ give 160–161° (15 mm.) for the same compound.

Anal. Calcd. for $C_4H_4SCl_6$: Cl, 71.67; S, 10.80. Found: Cl, 70.88, 70.85; S, 11.05, 10.93.

This compound, since it contains no hydrogen in the chlorinated ethyl group, is stable and distills unchanged. Further chlorination under the conditions employed by us leads to a complete breaking up of the molecule with the formation of chlorinated hydrocarbons. This was also observed by Mann and Pope.

Summary

1. Practically all of the compounds theoretically possible on treating β, β -dichloro-ethyl sulfide with chlorine have been isolated and identified.

2. With one exception, all chlorinated derivatives below the hexachloro are unstable, splitting out hydrogen chloride on distillation with formation of unsaturated compounds. The exception, $\alpha, \beta, \beta, \beta'$ -tetrachlorodiethyl sulfide, may be distilled, but breaks up like the others on refluxing.

3. None of these compounds is vesicant.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. III

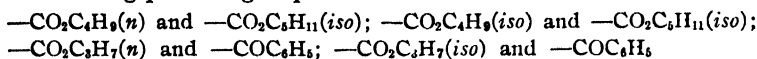
BY R. E. NELSON, N. W. SHOCK AND W. H. SOWERS

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Previous work published from this Laboratory¹ has shown that, "when *o*-aminophenol is acylated with the structural isomers, *n*-carbopropoxy and *isocarbopropoxy* groups, irrespective of their original positions, a partial rearrangement occurs. When the corresponding compounds with the *n*- and *isobutoxy* groups are made, their behavior is somewhat different. While the butyl carbonate of *isobutyl-o*-hydroxycarbanilate rearranges partially, giving a mixture of the two isomers, *isobutyl* carbonate of butyl *o*-hydroxycarbanilate was not found to change." In view of the behavior of these isomers against each other in the acylating of *o*-aminophenol it became of interest to us to investigate the behavior of such structural isomers against an aliphatic group and also against an aromatic group.

The following pairs of groups were used:



Iso-amyl-*o*-hydroxycarbanilate was acylated with *n*-butylchloro-carbonate and a stable diacyl obtained which yielded *iso*-amyl-*o*-hydroxycarbanilate on saponification. When *n*-butyl-*o*-hydroxycarbanilate was

¹ Nelson and Aitkenhead, *THIS JOURNAL*, **48**, 1680 (1926).

acylated with *iso*-amylchlorocarbonate the same diacyl was obtained as above and the saponification product was *iso*-amyl-*o*-hydroxycarbanilate. The *n*-carbobutoxy group in the second diacyl had migrated from the nitrogen to the oxygen during the preparation of the compound.

When *iso*-amyl-*o*-hydroxycarbanilate was acylated with *iso*-butylchlorocarbonate a stable diacyl was obtained which yielded *iso*-amyl-*o*-hydroxycarbanilate on saponification. Treatment of *iso*-butyl-*o*-hydroxycarbanilate with *iso*-amylchlorocarbonate resulted in the same diacyl as that from *iso*-amyl-*o*-hydroxycarbanilate and the saponification product was *iso*-amyl-*o*-hydroxycarbanilate. In this case the *iso*-carbobutoxy group had migrated from the nitrogen to the oxygen.

Benzoyl-*o*-aminophenol was acylated with *n*-propylchlorocarbonate and gave a diacyl which yielded benzoyl-*o*-aminophenol on saponification. When *n*-propyl-*o*-hydroxycarbanilate was acylated with benzoyl chloride the same diacyl was obtained and the saponification product was benzoyl-*o*-aminophenol. A rearrangement of the *n*-carbopropoxy from the nitrogen to the oxygen had taken place in the latter case.

When *isopropyl*-*o*-hydroxycarbanilate was acylated with benzoyl chloride a stable diacyl was obtained which yielded *isopropyl*-*o*-hydroxycarbanilate on saponification. Treatment of benzoyl-*o*-aminophenol with *isopropyl*chlorocarbonate yielded the same diacyl. Saponification gave *isopropyl*-*o*-hydroxycarbanilate. The benzoyl group had migrated from the nitrogen to the oxygen.

Experimental Part

All the mono-acyls used were prepared by Groenvik's method and are described in the literature.

The diacyl derivatives of *o*-aminophenol were prepared by the Schotten-Baumann method from the mono-acyl derivatives and the acyl chlorides as follows. About 3 g. of the mono-acyl derivative was dissolved in 75 cc. of water containing 1 g. of potassium hydroxide (slightly more than the calculated amount). After solution was complete, an excess (about 2 cc.) of the acyl chloride was added. The oil which formed was extracted with

TABLE I
DIACYL DERIVATIVES

Compound	Formula	M. p., °C.	Analysis, N, %	
			Calcd.	Found
Butylcarbonate of <i>iso</i> -amyl- <i>o</i> -hydroxycarbanilate	$C_4H_9CO_2OC_6H_4NHCOC_6H_{11}$	77	4.33	4.23
<i>iso</i> Butylcarbonate of <i>iso</i> -amyl- <i>o</i> -hydroxycarbanilate	$C_4H_9CO_2OC_6H_4NHCOC_6H_{11}$	61.5	4.33	4.38
Propylcarbonate of benzoyl- <i>o</i> -aminophenol	$C_3H_7CO_2OC_6H_4NHCOC_6H_5$	52	4.68	4.67
<i>o</i> - <i>iso</i> Carbopropoxyamino-phenylbenzoate	$C_3H_7CO_2NHC_6H_4OCOC_6H_5$	82	4.68	4.68

nation of the compounds has shown that this was in fact the case and that they contained the impurity when we received them. This is confirmed by the results obtained by Orndorff, Gibbs, McNulty and Shapiro and contained in a paper which has been submitted to THIS JOURNAL. When these substances are repurified with a fore-knowledge of the fact that they contain benzene, the impurity can be partially or wholly removed, with the result that the absorption pattern is either greatly diminished in intensity or entirely absent.

It seems desirable to know how benzene was introduced into these compounds. Letters from the leading manufacturers in answer to inquiries as to the possibility of diethyl ether containing a trace of benzene are about equally divided between those who cannot account for its presence and those who state frankly that ether is sometimes prepared from alcohol which has been denatured by benzene. To quote from the letter of one producer:

The Internal Revenue Bureau have authorized two special denatured alcohols for use in the manufacture of ether.

1.—S. D. Formula 2-B is made up as follows: "To 100 gallons of ethyl alcohol add $\frac{1}{2}$ gallon of benzol."

2.—S.D. 13-A is made up as follows: "To 100 gallons of ethyl alcohol add 10 gallons of sulfuric ether."

"We hold permits to use either of these formulas."

Over a period of about three years we continuously found the absorption bands not only in the U.S.P. ether but also in the C.P. anhydrous ether (distilled over sodium). During this period two different brands of diethyl ether were used with perfectly uniform results. Several brands now on the market do not show the impurity, including one of those in which the absorption was previously found. Some producers state they have not used alcohol denatured according to Formula 2-B during the past year. Since the methyl-*n*-amyl ether is prepared by use of the Grignard reaction, the trace of benzene in that substance can now be attributed to the anhydrous ether used in its preparation.

In the light of these facts we wish to raise two questions of general interest. The first is: How generally does benzene occur as an impurity in liquid organic compounds of highest quality? It would seem that since benzene is frequently used in the dehydration processes and also in the dehydration of many crude products, its presence must be suspected in all compounds prepared in this way. It now appears that it may also be introduced whenever commercial U.S.P. ether or C.P. anhydrous ether (distilled over sodium) is used in a preparation process. These two groups serve to bring a very large number of liquid organic compounds under the suspicion of containing benzene. Certainly the amount of impurity is no more than a trace, but the possibility of its presence should be generally recognized.

The second question is: Does anesthetic ether ever contain benzene? We have examined four brands of anesthetic ether. In only one case was an absorption pattern obtained and this was much fainter than has been found with U.S.P. ether or c.p. anhydrous ether containing the impurity.

The latter part of Dr. de Laszlo's article does not deal with a question of fact but rather with the interpretation of ultraviolet absorption spectra. Since the validity of the experimental results contained in our paper has been disproved, a further discussion of interpretation does not seem profitable at this time. However, on the basis of the quantum theory, we find little reason for supposing any absorption or emission spectrum to be essentially continuous.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF HYNSON, WESTCOTT & DUNNING]

SALICYLSULFONPHTHALEIN AND ITS TETRABROMO AND MONOMERCURY DERIVATIVES

BY WILTON C. HARDEN

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Since the synthesis of the first sulfonphthaleins by Remsen and his students¹ many new members of this class of compounds have been described by Orndorff and his co-workers,² Clark and Lubs,³ Cohen⁴ and others.

The purpose of the present paper is to describe still another sulfonphthalein, namely, salicylsulfonphthalein. The only mention of this compound in the literature is contained in some German patents⁵ describing certain dyestuffs prepared by the condensation of *o*-sulfobenzaldehyde with various phenols, cresols and substituted phenols and cresols. In this manner salicylic acid was condensed with *o*-sulfobenzaldehyde to give a red dye.

The author has prepared this compound by condensing salicylic acid with the anhydride of *o*-sulfobenzoic acid and found it to possess some interesting properties. Its tetrabromo and its monohydroxymercuri derivative have also been prepared and will be discussed.

Since nearly all of the sulfonphthaleins are useful indicators in the determination of hydrogen-ion concentration and since salicylsulfon-

¹ (a) Remsen, *Am. Chem. J.*, **6**, 180 (1884); (b) Remsen and Saunders, *ibid.*, **17**, 352 (1895); (c) Sohon, *ibid.*, **20**, 257 (1898).

² (a) Orndorff and Sherwood, *THIS JOURNAL*, **45**, 486 (1923); (b) Orndorff and Shapiro, *ibid.*, **46**, 2856 (1924); (c) Orndorff and Purdy, *ibid.*, **28**, 2212 (1926); and others.

³ Clark and Lubs, *J. Wash. Acad. Sci.*, **5**, 609 (1915); **6**, 481 (1916); **6**, 483 (1916).

⁴ (a) Cohen, *U. S. Public Health Reports*, **38**, 199 (1923); (b) **41**, 53, 3051 (1926).

⁵ Friedländer, (1908-1910), vol. 9, p. 195; D. R. P. 189,938-198,909 and others.

phthalein contains in addition to the sulfonic acid group two carboxyl groups, it was thought that a study of its color changes in solutions of varying P_H would be of interest. For this purpose a 0.1% solution in 70% alcohol was used. Five-tenths of a cc. of this solution was added to 10 cc. of various buffer mixtures prepared according to Clark.⁶ As would be expected the compound is an excellent indicator; it is yellow at all P_H 's below 6.6 and shades through a brown to a bluish red at P_H 8.2. The fact that at P_H 7.0–7.2 the color is distinctly brown, while below this point it is yellow and on the alkaline side red, should make the indicator a useful one in those cases where an indicator which shows a marked color change at the neutral point is desired. The color change of the tetrabromo derivative, that is, tetrabromosalicylsulfonphthalein, was determined in a similar manner. This indicator was found to change from a yellow at P_H 's lower than 3.2 through a brownish-purple to a clear purple at P_H 4.6. Color standards prepared using these indicators have shown no appreciable fading after several months' exposure to ordinary light. Since these compounds have at least a potential value as indicators, the author suggests that they be called, in accordance with the usual custom, Salicyl Red and Salicyl Purple in place of the longer salicylsulfonphthalein and tetrabromosalicylsulfonphthalein. No attempt has been made to determine the apparent dissociation constants or spectrophotometric data for these indicators.

The monohydroxymercuri derivative of the unhalogenated sulfonphthalein has also been prepared and the germicidal properties of the three compounds have been studied *in vitro*. The mercury derivative, as would be expected, is the only one to show any marked germicidal power.

Experimental Part

Preparation of Salicylsulfonphthalein (Salicyl Red).—The salicylic acid used was the ordinary U. S. P. variety. The anhydride of *o*-sulfobenzoic acid used was prepared by the method described by White and Acree.⁷ Fifty g. of salicylic acid was intimately ground in a mortar with 24 g. of the anhydride. This amount of salicylic acid represents about a 50% excess. This mixture was transferred to an Erlenmeyer flask, 2 cc. of concd. sulfuric acid and 10 cc. of fuming stannic chloride added and the flask heated in an oil-bath for four hours at 120–130°. At this temperature the mixture slowly melts and begins to redden. At the end of four hours the temperature was raised slowly (1/2 hour) to 160–180°. At this temperature the melt becomes more intense in color and begins to harden. The temperature was kept at 170° for several hours longer and the semi-fused mass then poured into 4 liters of hot water. If the melt is allowed to cool it becomes caked and great difficulty is experienced in removing it from the flask. Sodium carbonate was then added until the solution was alkaline. Since the dye is a relatively strong acid, care must be taken in this operation to prevent the solution

⁶ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1922, 2nd edition.

⁷ White and Acree, *THIS JOURNAL*, 41, 1190 (1919).

from frothing over. The purple alkaline solution was next heated to boiling and filtered while hot. It was then transferred to a large evaporating dish, strongly acidified with hydrochloric acid and concentrated on the water-bath. Some of the dye separates out at this stage as a green tar and should be removed, redissolved in sodium carbonate and reprecipitated. After several such treatments the dye is obtained in a pure form as a red, amorphous powder. The main body of the solution was evaporated to about one-third of its original volume and allowed to cool. The dye separates from this solution contaminated with large amounts of salicylic acid. This was removed by repeated extractions with ether, in which the dye is insoluble. The dye was then further purified by repeated solution in sodium carbonate and reprecipitation with hydrochloric acid.

Anal. Calcd. for $C_{21}H_{14}O_6S$: S, 7.24. Found: 7.38.

Preparation of Tetrabromosalicylsulfonphthalein (Salicyl Purple)—4.5 g. of Salicyl Red prepared as described above was suspended in 100 cc. of glacial acetic acid and a solution of 7.0 g. of bromine in glacial acetic acid added. The solution was warmed on the steam-bath for several hours and allowed to stand overnight. The next day it was again warmed on the steam-bath and aspirated while warm to remove hydrobromic acid and some of the acetic acid. This is essentially the method described by Cohen^{4a} for the preparation of tetrabromo-*m*-cresolsulfonphthalein. When the solution had been evaporated to about one-half its original volume, it was cooled in the ice-box for several hours, when a small crop of crystals separated. These were filtered off and the filtrate poured into dilute hydrochloric acid. The dye separated as an amorphous, yellow powder which was dissolved in sodium carbonate, reprecipitated, dried and analyzed.

Anal. Calcd. for $C_{21}H_{10}O_6Br_4S$: Br, 42.18; S, 4.20. Found: Br, 42.20; S, 4.52.

Preparation of Monohydroxymercuri-salicylsulfonphthalein.—4.4 g. of Salicyl Red was dissolved in sufficient normal sodium hydroxide to form the disodium salt. To this solution was added a solution of 3.18 g. of mercury acetate to which had been added several drops of acetic acid. There was no apparent action in the cold and no precipitation of the mercury salt of the dye. If such a salt is formed in this case, it is probably soluble. The solution was boiled for several hours when it lost its red color and became quite brown. The boiling was continued until a small test-tube portion showed no free mercury when tested with ammonium sulfide. It was then filtered and poured into dilute hydrochloric acid. The mercurated material came down at once as a brown powder which was filtered by suction and washed repeatedly with warm water.

Anal. Calcd. for $C_{21}H_{14}O_6SHg$: Hg, 30.4. Found: Hg, 29.84.

Bacteriological and Pharmacological Part

The method used for testing the germicidal properties of these compounds was a modification of the Hygienic Laboratory method for determining phenol coefficients. The procedures used are, briefly, as follows: 0.1 cc. of a twenty-four hour broth culture of the test organism is added to 5 cc. of the diluted sample at 37°. Body temperature is used because of the possible application of these materials for combating infections within the human body. At the end of one, five and fifteen minutes, subculture was made into 10 cc. of sterile broth and this incubated at 37° for forty-eight hours, at which time they were observed for growth. It was found that a 1% solution of the mercurated salicylsulfonphthalein kills *B. Typhosus* and *Staph. Aureus* within one minute. It also kills

B. Typhosus in 1-1000 dilution within five minutes and in 1-2000 dilution within fifteen minutes. *Staph. Aureus* is killed by a 1-500 dilution within five minutes but is not killed by 1-1000 dilution in fifteen minutes. One per cent. solutions of Salicyl Red and Salicyl Purple do not kill either *B. Typhosus* or *Staph. Aureus* in fifteen minutes under the same conditions.

A preliminary pharmacological investigation shows that the mercurated derivative apparently is eliminated from the body through the digestive system, while the other two compounds, like most sulfonphthaleins, are eliminated through the urinary tract.

The author wishes to express his thanks to Drs. G. F. Reddish and David L. Macht for the bacteriological and pharmacological investigation of these compounds.

Summary

1. Salicylsulfonphthalein (Salicyl Red) has been prepared and its indicator properties have been studied.

2. Tetrabromosalicylsulfonphthalein (Salicyl Purple) has been prepared and its indicator properties have been studied.

3. The monohydroxymercuri derivative of salicylsulfonphthalein has been prepared.

4. A preliminary bacteriological and pharmacological study of these compounds has been made.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE ALKYLATION OF BENZENE, TOLUENE AND NAPHTHALENE

By T. M. BERRY¹ AND E. EMMET REID

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It was shown by Balsohn² that ethylene may be substituted for ethyl chloride in the Friedel and Crafts synthesis. Milligan and Reid³ found that the reaction is facilitated by high-speed stirring to such an extent that this becomes a convenient method for the ethylation of benzene.

The present investigation has to do with a further study of the reaction and with its extension to propylene and cyclohexene.

The ethylene (or propylene) is passed into the benzene at such a rate that only an occasional bubble escapes. If an excess of gas passes through, hydrogen chloride is carried away and the reaction slows down. It is

¹ From the Ph.D. dissertation of T. M. Berry, June, 1923.

² Balsohn, *Bull. soc. chim.*, [2], 31, 539 (1879).

³ (a) Milligan and Reid, *THIS JOURNAL*, 44, 206 (1922); (b) *Ind. Eng. Chem.*, 15, 1048 (1923).

usually possible to restore the original speed by passing in a small amount of dry hydrogen chloride.

In the ethylation of benzene, ethylene is not to be considered as simply a substitute for ethyl chloride. For every molecule of ethyl chloride that reacts, one of hydrogen chloride is eliminated. This escaping as a gas carries off with it much of the volatile ethyl chloride. The utilization of ethyl chloride depends on the rate at which it is passed. At 0.01 mole per minute per mole of benzene only 25% of it reacts, while at one-fourth of this rate 43% reacts. Ethylene may be completely absorbed at these rates.

Drying the benzene with sodium gave decidedly better results than using only calcium chloride. The runs were made at about 70°, though there appears to be little difference in the rate between 60° and 90°. There is usually an incubation period of about twenty minutes before much ethylene is absorbed. Refluxing for several minutes appears to shorten this. The addition of 10% of higher ethylated benzenes from a previous run may hasten the starting of the reaction. The speed increases with the accumulation of ethylated benzenes, reaching a maximum when about 4 equivalents of ethylene have been absorbed, remaining nearly constant for a while and then declining.

The apparatus used was that described by Milligan and Reid,^{8b} the stirrer being run at 7000 to 8000 r.p.m.

As is well known, all of the possible ethylation products are formed and no way has been found of directing the process to the production of any one, exclusively. Some hexa-ethylbenzene is present when less than 0.5 mole of ethylene has been absorbed and less than half of the benzene has been attacked. Data from a number of runs are given in the experimental part. As the conditions under which the runs were made were not all the same and as the separations were made by fractionation the figures are not strictly comparable or very exact but these conclusions may be drawn. As the reaction progresses, mono-ethylbenzene increases regularly to about 30% when about 1.1 mole of ethylene has been passed in. Diethyl- and tetra-ethylbenzene never go much above 20%. The penta-ethyl is present almost from the first but its concentration is remarkably low and nearly constant to the end. There seems to be a preferential formation of the triethyl which constitutes over 50% of the mixture when somewhat over 3 moles of ethylene have reacted. In subsequent work as high as 80% of triethyl has been found. Hexa-ethyl benzene appears early and always exceeds the tetra- or penta-. It steadily increases until it constitutes nearly 90% of the mixture, when the mixture becomes too nearly solid to stir. There is no difficulty in preparing hexa-ethylbenzene in one operation; but on account of the large increase in volume it is usually more convenient to stop the reaction when three equivalents of ethylene have been introduced, separate and use this material for a new run.

The best proportion of aluminum chloride seems to be 1 mole (AlCl_3) to about 13 of benzene. When the stirring is stopped the reaction mixture separates sharply into two layers. The top one is clear and colorless and contains only a trace of aluminum chloride. The lower layer is dark and viscous and consists of aluminum chloride associated with something like its own weight of hydrocarbons. In a few runs this lower layer has been worked up separately. As the amount of this layer is relatively small the results on it are not as exact as could be desired but they do show that each of the hydrocarbons present is partitioned between the two layers and that the aluminum chloride holds the higher ethylated benzenes in preference to the lower. From mono- to tetra-ethylbenzene the concentrations in the two layers do not differ greatly but there is a marked heaping up of penta-ethylbenzene in the lower layer which always contains more of it than of either the tetra- or hexa-. The hydrocarbon which is most abundant in the lower layer always contains one or two more ethyl groups than the one that predominates in the upper. Toluene is more readily ethylated than benzene, and bromobenzene less so. Both give complicated mixtures which contain the expected products.

Gustavson⁴ prepared *isopropylbenzene* from propyl bromide and benzene in the presence of aluminum chloride with 34% yield. Propylene does not seem to have been used for this purpose. Propylene is taken up by benzene under the same conditions as ethylene but only about 4% as rapidly. The product separates into two layers, the lower being relatively larger and slower to react with water than in the ethylation of benzene. It was impracticable to carry the fractionation above 290° as the residue above this was a tarry mass. Hence the propylated benzenes were separated only as far as the tetra-. From some of the higher fractions a well crystallized solid separates, m. p. 117° and b. p. 260° at 775 mm. This appears to be 1,2,4,5-tetra-*isopropylbenzene*. Of the di-*isopropylbenzenes* the meta seems to predominate, as does the symmetrical among the tri-.

As in ethylation the rate increases as propylation progresses. With mono-*isopropylbenzene* it is double and with the tri- it is 10 times what it is with benzene.

A curious phenomenon is the formation of two aliphatic hydrocarbons, b. p. 28° ; d_4 0.7095 and the other b. p. $56\text{--}59^\circ$. The latter is probably di-*isopropyl*.

Toluene is more readily propylated than benzene, the chief product seeming to be *p*-cymene. Naphthalene was propylated by the transfer of *isopropyl* groups from di-*isopropylbenzene*.

Cyclohexane reacts with benzene when aluminum chloride is added to a mixture of the two. Some cyclohexylbenzene is obtained but the most

⁴ Gustavson, *Ber.*, 11, 1251 (1878).

of the product is high boiling. The results are similar to those obtained by Kursanoff,⁵ who used cyclohexyl chloride.

Experimental

The details of the runs with ethylene are given in the table below. The regular amount of benzene was 300 g., 3.85 moles, but 455 g., 5.83 moles, was used in Runs 4 and 5. In Run 10, 363 g., 2.24 moles, of triethylbenzene was used instead of benzene as starting material and similarly 300 g., 2.24 moles, of diethylbenzene in Run 11. The ethyl groups in these were counted in calculating the ratio of ethylene to benzene. The rate of stirring was 7200 to 8200 r.p.m. The ethylene put in is in moles per mole of benzene. The largest amount of ethylene put in during a run was 352 l. in 675 minutes in Run 9. The highest rate was in Run 11, 402 cc. per minute per mole. At the end of a run the product was drowned, the oil layer washed, dried and fractionated through a Vigreux column. The results are given in the following tables.

TABLE I
COMPOSITION OF PRODUCT IN MOLES PER 100 MOLES OF BENZENE

Run	Moles of ethylene	Benzene	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-
1	0.20	87.9	10.9	1.24
2	0.50	80.8	15.5	2.14	0.67	0.15	0.06	0.67
3	0.56	80.5	15.2	1.67	0.71	1.91
4	1.14	31.6	35.2	21.1	4.0	2.4	2.8	2.82
5	1.19	31.0	36.9	22.7	5.1	1.8	1.2	1.16
6	1.27	49.6	26.7	11.2	3.9	1.2	0.60	6.7
7	1.38	37.3	30.1	11.6	6.7	3.00	3.2	8.2
8	1.68	35.4	23.4	13.6	6.3	4.2	3.6	13.4
9	3.66	0.2	1.1	10.6	56.2	11.6	1.5	18.7
10	5.24	7.00	18.8	2.4	71.8
11	5.74	8.5	0.9	90.6

TABLE II
COMPOSITIONS OF THE TWO LAYERS IN MOLAR PER CENT.

Run	Ethylene	Layer	Benzene	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-
5	1.19	Upper	32.3	37.7*	21.7	4.6	1.8	0.9	1.0
		Lower	5.0	22.3	43.3*	15.5	3.8	6.7	3.4
		Ratio	0.16	0.6	2.0	3.4	2.1	7.1	3.4
7	1.38	Upper	39.7*	28.8	10.9	6.7	2.8	1.8	9.2
		Lower	..	45.8*	20.8	2.8	4.6	22.2	3.7
		Ratio	..	1.6	1.9	0.4	1.6	12.2	0.4
8	1.68	Upper	35.4*	22.6	13.6	6.0	4.0	5.0	13.4
		Lower	17.6	22.0*	6.6	7.7	4.9	35.2*	6.0
		Ratio	0.5	1.0	0.5	1.3	1.2	7.0	0.5
9	3.66	Upper	.2	1.1	10.6	55.5*	12.0	1.3	19.3
		Lower	4.6	33.8	19.0	42.2*	0.4
		Ratio	0.4	0.6	1.6	33	.02

⁵ Kursanoff, *Ann.*, 318, 310 (1901).

In four of these runs the two layers were separated and worked up separately. The compositions of the upper and lower layers and their ratios are given in Table II.

On account of the smallness of the amounts of the hydrocarbons in the lower layers, the figures for the lower layers are not as accurate as for the upper. Run 8 showed a high percentage of the penta- in both layers. The highest in each layer is starred. The relative weights of the hydrocarbons in the two layers were 16, 12, 12 and 13 to 1.

The Ethylation of Toluene.—Ethylene was passed into 280 g., 3.04 moles, of toluene under the usual conditions. Absorption was at the rate of 266 cc. per minute per mole of toluene and 0.9 equivalent was taken up in 81 minutes. Distillation of the product gave the following.

TABLE III
PRODUCTS FROM THE ETHYLATION OF TOLUENE

Boiling range, °C.	Weight, g.	Probable constituents
Up to 120	45	Toluene
120–145	42	Ethylbenzene and xylenes
145–164	121	Ethyltoluenes
164–207	93	Higher substitution products
Above 207	5	Higher substitution products

The part boiling from 198–203° was strongly fluorescent.

The Ethylation of Bromobenzene.—Into 484 g., 2.83 moles, of bromobenzene containing 0.37 mole of aluminum chloride one equivalent of ethylene was passed. It was taken up at the rate of 70 cc. per mole per minute.

Distillation of the product gave the following.

TABLE IV
PRODUCTS FROM THE ETHYLATION OF BROMOBENZENE

Boiling range, °C.	Weight, g.	Probable constituents
Up to 140	15	Benzene and ethylbenzene
140–180	135	Ethyl- diethylbenzenes
180–215	86	Brominated ethylbenzenes
215–250	115	Brominated ethylbenzenes
Above 250	85	Tarry residue

At 240–250° decomposition began with evolution of hydrobromic acid.

The Propylation of Benzene.—Propylene was made by dropping *iso*-propyl alcohol⁶ on to metaphosphoric acid heated to 500° or above. This method gives an excellent yield of pure propylene but is troublesome on account of the destructive action of the phosphoric acid on the Pyrex flask. Propylene was also prepared by passing the *isopropyl* alcohol vapor over pumice impregnated with alumina and kept at 600°. The propylene was collected over water and purified as was the ethylene.

⁶ Our thanks are due to the Standard Oil Co. of N. J. for a generous supply of *isopropyl* alcohol.

The runs with propylene were in every way similar to those with ethylene but were less numerous. Two runs were made starting with benzene, two with mono-*isopropyl*benzene and one with tri-*isopropyl*benzene. The distillations of the products were stopped at about 280°, as above that temperature decomposition seemed to set in. The penta- and hexa-*isopropyl*benzenes, if they were formed, were left in the residue.

The reaction product separates into two layers as in the ethylation of benzene, but with propylene the lower layer is relatively larger and the aluminum chloride complexes which it contains are decomposed by water more slowly than are those obtained in the ethylation of benzene. Usually only about three-fourths of the hydrocarbons contained in it boil below 285°.

For four runs the compositions of the product in percentages by weights were:

TABLE V
PRODUCTS FROM THE PROPYLATION OF BENZENE, PERCENTAGE BY WEIGHT

No.	Moles of propylene	Benzene	Mono	Di-	Tri-	Tetra-	Residue
1	0.6	16.3	42.5	27.0	6.1	2.1	6.1
2	0.75	18.9	52.0	20.0	3.0	1.3	4.8
3	1.97	1.4	0.6	3.9	87.6	3.3	3.3
4	1.93	1.3	15.6	46.7	31.0	5.4	...

In three of these runs the two layers were worked up separately with the following results.

TABLE VI
COMPOSITIONS OF THE TWO LAYERS IN PERCENTAGES BY WEIGHT AND THEIR RATIOS

Run	Propylene	Layer	Benzene	Mono-	Di-	Tri-	Tetra-	Residue
1	0.6	Upper	15.7	45.9	30.8	5.2	1.2	1.2
		Lower	18.8	28.6	11.1	9.7	5.6	26.1
		Ratio	1.2	0.62	0.36	1.9	4.7	22
2	0.75	Upper	19.2	55.0	22.4	2.2	..	1.2
		Lower	17.4	32.6	9.9	6.6	1.6	25.3
		Ratio	0.9	0.59	0.44	3.0	..	21
3	1.97	Upper	1.5	0.5	4.2	88.7	3.0	2.1
		Lower	..	1.1	1.1	71.7	15.2	10.9
		Ratio	..	2.2	0.25	0.9	5.1	5.2

In these runs the relative weights of the hydrocarbons in the upper and lower layers were 3.5, 4.5 and 10.3 to 1.

The product from Run 4 was fractionated repeatedly. The final results were as follows.

The indications are that about 65% of the di-*isopropyl* is the meta and that the 1,3,5-tri-*isopropyl* is about 75% of that group.

It was found particularly easy to propylate the tri-*isopropyl*benzene fraction; 250 g. of it took up 56 liters of propylene in twelve hours. On cooling,

TABLE VII
 FRACTIONATION OF THE PRODUCT FROM RUN 4

Temp. range, °C.	Weight, g.	Probable constituents
Up to 75	17	Aliphatic hydrocarbons
75 - 90	20	Benzene
152 -156	220	<i>Isopropylbenzene</i>
150 -201	25	Mono- and di-
201 -203.5	33	<i>m</i> -Di- <i>isopropylbenzene</i>
203.5-204.5	410	<i>m</i> -Di- <i>isopropylbenzene</i>
204.5-208.5	68	Mixture
208.5-209.5	119	Di- <i>isopropylbenzene</i> (?)
209.5-233	84	Mixture of di- and tri-
233.5-234.5	256	1,3,5-Tri- <i>isopropylbenzene</i>
234.5-246	164	Tri- <i>isopropylbenzenes</i>
Above 246	61	Tetra- and higher

the product solidified, and by centrifuging white crystals were obtained. After several recrystallizations from alcohol this material melted at 117° and boiled at 260° under 775 mm. Some of it was oxidized by long heating with potassium permanganate solution and an acid obtained which melted at 282°. Mellitic acid melts at 286° and the di-anhydride of 1,2,4,5-benzenetetracarboxylic acid melts at the same temperature. The hydrocarbon is probably the 1,2,4,5-tetra-*isopropylbenzene* as its boiling point, 260°, seems much too low for the hexa-*isopropyl*. Hexa-ethylbenzene boils at 294° and the hexa-*isopropyl* should boil at least that high. The 1,2,4,5-tetramethylbenzene is a solid and boils below its isomers.

 TABLE VIII
 ANALYSIS OF THE HYDROCARBON

	Found, %		Calculated for		Hexa-
Carbon	87.43	87.60	Tetra- 87.72	Penta- 87.41	87.18
Hydrogen	12.43	12.61	12.28	12.59	12.82

Assuming that the carbon found is low and the hydrogen high the analysis indicates the tetra-.

By repeated fractionation a quantity of 1,2,4-tri-*isopropylbenzene* was separated. It boils at 237-237.5° at 752 mm., 97-97.5° at 4 mm.; d_4^{20} 0.8764 and d_{25}^{25} 0.8593, N_D 1.4855 at 25°. It was identified by oxidation to an acid which melted, with formation of the anhydride, at 214°, which corresponds to the 1,2,4-benzenetricarboxylic acid.

The oils boiling below 75° were refractionated and separated into two hydrocarbons, one boiling at 28°, d_4^{20} 0.7095 and the other boiling at 56-59°. The latter is evidently di-*isopropyl*, which boils at 58°.

The Propylation of Toluene.—Toluene reacted somewhat faster than did benzene under the same circumstances. From 662 g. of toluene which had taken up 0.3 equivalent of propylene the following fractions were obtained.

TABLE IX

PROPYLATION OF TOLUENE		
Boiling range, °C.	Weight, g.	Probable constituents
Up to 105	5	Benzene
105-120	370	Toluene
120-145	17	Xylenes
145-170	25	Tri-ethylbenzene and cymenes
170-185	161	<i>m</i> - and <i>p</i> -Cymenes
Above 185	60	

As the cymenes boil too close together for fractionation, advantage was taken of the fact that their bromine derivatives boil 10° apart, that of the meta at 224° and that of the para at 234°. A portion of the 170-185° fraction was brominated and 80% of the product was found to boil between 228° and 240°, indicating a preponderance of the *p*-cymene.

The Propylation of Naphthalene.—Naphthalene was stirred with di-*isopropyl*benzene in the presence of aluminum chloride. From 217 g. of naphthalene and 132 g. of di-*isopropyl*benzene at 90° for 4.5 hours, 15 g. of a fraction boiling at 264-266° was obtained. This was probably *isopropyl*naphthalene. One third of the naphthalene was recovered unchanged and there were higher-boiling products which were not identified.

Cyclohexene and Benzene.—As cyclohexene resembles ethylene in many respects, it was thought that it should react with benzene under the usual conditions to give cyclohexylbenzene. To a mixture of 276 g. of benzene and 290 g. of cyclohexene, 60 g. of aluminum chloride was added. Even without stirring a violent reaction took place. Stirring for thirty seconds would bring the mixture to a boil. After a time the mixture could be stirred continuously. This was done for five hours, during which time the temperature remained at about 55°. The mixture was worked up as usual and gave 50 g. of cyclohexylbenzene, boiling from 230-245°, besides large amounts of high-boiling products. Kusanoff⁶ got similar results using cyclohexyl chloride.

Summary

The ethylation of benzene by ethylene in the presence of aluminum chloride with high-speed stirring has been studied. The ethylbenzenes from mono- to hexa- are readily obtained, their relative amounts depending on the proportion of ethylene taken up. Similar results were obtained using propylene. Cyclohexene also reacts with benzene under the same conditions. Toluene and naphthalene may be substituted for the benzene.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

SOME DERIVATIVES OF ETHYLBENZENE¹BY E. L. CLINE² AND E. EMMET REID

RECEIVED AUGUST 29, 1927

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Because of the close structural relationship to benzene and toluene, ethylbenzene has been a subject for investigation by several workers. These, however, had small quantities of material and many discrepancies are evident in the records of their results.

Recent researches^{3,4} have led to the development of a method for the production of ethylbenzene in large quantities. We, therefore, undertook the preparation of some new derivatives of ethylbenzene in order to make further comparisons and at the same time to straighten out the literature on some of the previously prepared compounds.

Historical

Beilstein and Kuhlberg,⁵ two of the earliest workers in this field, found an almost complete analogy between the nitro and amino compounds of toluene and ethylbenzene. Vorländer⁶ found that ethylbenzene acts more like benzene than toluene when treated with hydrocyanic acid, cyanogen, acid chlorides and acid cyanides. The same author further states that ethylbenzene does not react to give an aldehyde by the Gattermann-Koch synthesis, in which statement he is corroborated by several other investigators. However, J. von Braun and Hans Engel⁷ report the preparation of *p*-ethylbenzaldehyde by means of this reaction, so that, in this case, ethylbenzene reacts more like toluene than benzene.

Schultz and Flachsländer⁸ prepared a series of dyes of the Congo type from benzidine, toluidine and the corresponding ethylbenzene base. They found that the Congo type prepared from diethylbenzidine had a greater solubility, greater coloring power but less resistance to light than that from the other two benzidines. However, they stated that the actual differences were very small.

Beilstein and Kuhlberg,⁵ Schultz and Flachsländer⁸ and Béhal and Choay⁹ have studied the nitration of ethylbenzene and the separation of *o*- and *p*-nitro-ethylbenzenes. Beilstein and Kuhlberg attempted to separate the two isomers by differences in their melting points. After twenty

¹ Read at the Baltimore meeting of the American Chemical Society, April, 1925.

² From the Ph.D. dissertation of E. L. Cline, Johns Hopkins University, 1925.

³ Milligan and Reid, *THIS JOURNAL*, **44**, 206 (1922).

⁴ Berry and Reid, *ibid.*, **49**, 3142 (1927).

⁵ Beilstein and Kuhlberg, *Ann.*, **156**, 206 (1870).

⁶ Vorländer, *Ber.*, **44**, 2461 (1911).

⁷ Von Braun and Engel, *Ann.*, **436**, 299 (1924).

⁸ Schultz and Flachsländer, *J. prakt. Chem.*, [2] **66**, 160 (1902).

⁹ Béhal and Choay, *Bull. soc. chim.*, [3] **11**, 208 (1894).

fractionations, they were not successful in getting complete separation, since the melting points are only nine degrees apart in contrast to the corresponding nitrotoluenes, where there is a difference of 61.5°. Schultz and Flachsländer fractionated eighty times in a vacuum in two-degree cuts to get two fractions 220–230° and 245–250° with a small intermediate fraction. Then they fractionated one hundred times at atmospheric pressure to obtain constant-boiling fractions at 223–224° for the *ortho* and 241–242° for the *para* isomer. Even with this painstaking procedure, the boiling points of the two isomers are wrong, due, perhaps, to defective thermometers.

The Present Investigation

The ethylbenzene was prepared according to a modification of the method of Milligan and Reid.³ Purified ethylene was introduced into benzene containing aluminum chloride, the mixture being stirred at the rate of 11,000 r.p.m. by a Witt stirrer, as described by Milligan and Reid.¹⁰

These investigators found that an "incubation period" of an hour or more was necessary to secure maximum absorption of the ethylene, whereas, if they used some of the higher ethylated benzenes (tri- to hexa-ethylbenzene), along with the above ingredients, the rate of absorption of the ethylene was greatly increased. With these facts in view, a process was worked out by which about 50% of the benzene used could be directly converted into ethylbenzene or, by returning the higher ethylated benzenes to the reaction flask, practically all of the benzene can be converted into ethylbenzene, due to the transfer of the ethyl groups from the higher alkylated ethylbenzenes to the free benzene.¹¹

Ethylbenzene was nitrated below 40°, thus avoiding to a large extent the formation of higher nitrated products. Instead of using the tedious method of fractional crystallization, as carried out by Schultz and Flachsländer, we built a high-precision vacuum still, similar to that described by Peters and Baker.¹²

Instead of the main outer glass jacket, we used a brass tube 5 cm. in diameter which was connected to two lead tubes leading to and from a xylene reservoir. The temperature of this jacket was maintained at about 140° by the boiling xylene instead of being electrically heated as described by the authors mentioned above. Except for some other minor details, the still was as described by Peters and Baker. By means of this still we were able to separate the *o*- and *p*-nitro-ethylbenzenes sharply by one distillation. This avoided high temperatures as well as loss of time and materials by repeated fractionation.

Beilstein and Kuhlberg obtained equal parts of the two nitro isomers,

¹⁰ Milligan and Reid, *Ind. Eng. Chem.*, **15**, 1048 (1923).

¹¹ Anschütz and Immendorff, *Ber.*, **18**, 657 (1885).

¹² Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

Schultz and Flachsländer report two parts of the *ortho* to one of the *para*, while Behal and Choay found one and a half parts of the *ortho* to one of the *para*. Our results averaged one and two-tenths parts of the *ortho* to one of the *para*. The boiling point of *o*-nitro-ethylbenzene is 135° at 37 mm. and that of *p*-nitro-ethylbenzene 154° at the same pressure.

Both the *o*- and *p*-nitro-ethylbenzenes are quite difficult to reduce to the corresponding amines. All of the earlier workers used tin and hydrochloric acid for both of these reductions but none of them report anything concerning the ease of reduction or the yields obtained. According to our observations this method is excellent in working with the *para* compound, the yield being about 90%, but with the *ortho* compound the yields are poor, probably on account of the entrance of chlorine into the ring as is the case in the reduction of *o*-nitrotoluene.^{13,14} The *para* isomer gives yields up to 80% with iron filings and hydrochloric acid but it is almost impossible to effect a complete reduction of the *ortho* isomer with these reagents. Ammonium sulfide in boiling alcohol solution is a good reducing agent for the *para* compound but is very slow with the *ortho*.

The reduction of 2,4-dinitro-ethylbenzene with ammonium sulfide has been studied by Schultz,¹⁵ who claimed to have obtained the 2-nitro-4-amino-ethylbenzene which had a melting point of 43°, with an acetyl derivative melting at 101°. We obtained proof that this reduction yields a mixture of 2-nitro-4-amino-ethylbenzene and the isomeric 2-amino-4-nitro-ethylbenzene. The former is an orange-yellow, crystalline solid which, after recrystallizing from alcohol, melts at 45° and gives an acetyl derivative melting at 110°. We were unable to isolate the latter in the pure form but we were successful in proving its presence by diazotizing a portion of the isomeric nitro-amino compounds and replacing the diazonium group with hydrogen. The products, *o*- and *p*-nitro-ethylbenzenes, were treated with zinc and hydrochloric acid, which would reduce the *para* and not affect the *ortho* isomer. The *p*-amino-ethylbenzene was separated from the *o*-nitro-ethylbenzene and an acetyl derivative prepared which, when recrystallized from water, melted at 94.5°, which is the melting point given for 4-acetyl-amino-ethylbenzene.

With these facts in view, there is little doubt that the low melting point given by Schultz for 2-nitro-4-acetyl-amino-ethylbenzene was due to the presence of an isomer.

The reduction of 2,4-dinitrotoluene with ammonium sulfide gives two isomers also, but due to the difference in stability of their hydrochlorides both have been isolated. We tried to separate the isomeric aminonitro-

¹³ Bamberger, *Ber.*, 28, 251 (1895).

¹⁴ Hurst and Thorpe, *J. Chem. Soc.*, 107, 934 (1915); *C. A.*, 9, 2887 (1915).

¹⁵ Schultz, *Ber.*, 42, 2634 (1909).

ethylbenzenes by the same method but, due to the small percentage of 2-amino-4-nitro-ethylbenzene, which gives the less stable hydrochloride, we were unable to obtain it in the pure form.

From the *o*- and *p*-amino-ethylbenzenes, a number of derivatives have been prepared and their properties studied; among these is a series of azo dyes prepared from aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline. The purpose in making these dyes was to determine the effect of the ethyl groups in comparison with the methyl group.

A distinct deepening in color is noticed in going from aniline to the methylaniline dye and a slight deepening in going from methylaniline to ethylaniline. In both the methylaniline and the ethylaniline series, the *para* isomer gives deeper shades than the *ortho*.

Experimental

Ethylbenzene.—Into a mixture of 300 g. (3.84 moles of benzene), 100 g. of higher ethylated benzenes, 15 g. of aluminum chloride (0.056 moles) and the lower layer from a previous experiment, three equivalents of ethylene were introduced in the course of two hours, the temperature being held between 70 and 80°. The ethylene was passed under the head of the Witt stirrer which was running at 11,000 r.p.m. After the addition of the ethylene, the reaction mixture was allowed to settle. It separated into two distinct layers, the top containing practically all of the hydrocarbons with a very little aluminum chloride and the lower which contained nearly all of the catalyst. This was left in the flask for the next run. The top layer was siphoned off, poured onto ice, washed and dried over calcium chloride and fractionated through a 90cm. punched-in column. By the first distillation it was divided into four fractions: one boiling between 80 and 100°, which was returned to the reaction vessel as benzene; one boiling from 100–150°, the ethylbenzene fraction; one boiling between 150 and 190°, the diethylbenzene fraction and a residue which was returned to the reaction vessel as higher alkylated benzenes. The ethylbenzene and the diethylbenzenes were purified in one distillation by passing them through the high-precision still. After purification, ethylbenzene boiled at 135°. Treating 300 g. of benzene with three equivalents of ethylene, the averages for seven runs were: recovered benzene 29 g., ethylbenzene 215 g., diethylbenzene 105 g., residue 39 g.

***o*- and *p*-Nitro-ethylbenzene.**—Into 700 g. (6.6 moles) of ethylbenzene, contained in a two-liter flask cooled by ice, a mixture of 510 g. of concd. nitric acid (sp. gr. 1.42) and 675 g. of concd. sulfuric acid was allowed to flow, dropwise, in the course of six hours. The contents of the flask was agitated with a Witt stirrer, revolving at 3000 r.p.m. and the temperature kept below 40°. After the addition of the acid, the mixture was stirred for three hours at room temperature and then the temperature was gradually raised to 100° in the course of four hours and kept there for two hours. The product was allowed to settle and the oil separated from the excess acid. The oil was washed several times with water, then with caustic soda solution and finally with water. It was distilled with steam in order to separate the mononitro-ethylbenzenes from the higher nitrated products. The oil remaining in the flask was principally 2-4-dinitro-ethylbenzene, previously described by Weisweiler.¹⁶

The oil volatile with steam was dried over calcium chloride and fractionated, using the high-precision vacuum still. The entire inner column was kept at 140° by the xylene vapors in the jacket. In the distilling flask was placed 760 g. of the nitro-ethylbenzenes

¹⁶ Weisweiler, *Monatsh.*, 21, 39 (1900).

and the pressure of the whole system brought to 37 mm. At this pressure the *o*-nitro-ethylbenzene distils at 135° while the *para* isomer boils at 154°. The water in the dephlegmator was regulated so that nine-tenths of the vapors was condensed. After practically all of the *ortho* compound has passed over the distillation ceases. At this point a cut is made. The liquid in the receiver is pure *o*-nitro-ethylbenzene, amounting to 384 g. The distillation is again resumed at 30 mm. and continued until the rate of distillation again slows down, when the pressure is lowered a few more millimeters. This process is continued until the temperature remains constant during the distillation of 30 cc., when it is stopped. The intermediate fraction (60 g.) is a mixture while that in the distillation flask is pure *p*-nitro-ethylbenzene (317 g.). Thus we were able to secure in the pure form 50.5% of *o*- and 41.7% of *p*-nitro-ethylbenzene.

Reduction of *p*-Nitro-ethylbenzene.—A mixture of 120 g. of granulated zinc and 75 g. of *p*-nitro-ethylbenzene was placed in a two-liter flask equipped with an air condenser. To this was added 250 g. of concd. hydrochloric acid in small portions, heat being applied at intervals. After all of the acid had been added, the mixture was heated on a water-bath for two hours to complete the reaction. The mixture was then made strongly alkaline with caustic soda and steam distilled. The distillate was saturated with salt, extracted with ether and the resulting solution dried and distilled; yield, 90%.

By reduction with iron filings and 10% hydrochloric acid, a yield of 80% was obtained.

Reduction of *o*-Ethyl-benzene.—Tin and hydrochloric acid gave a yield of 70% of *o*-nitro-ethylbenzene. With iron filings and 10% hydrochloric acid the reduction was not complete in sixteen hours at 130° so this method was abandoned.

Reduction of 2,4-Dinitro-ethylbenzene.—A solution of 50 g. of 2,4-dinitro-ethylbenzene in 150 g. of ethyl alcohol was treated with 150 g. of concd. ammonia water. The mixture was then alternately saturated with hydrogen sulfide and boiled until a gain in weight of 30 g. was effected. The solution was poured onto ice and the amine separated out. It was filtered off and dissolved in dilute hydrochloric acid. The acid solution was boiled with animal charcoal, filtered and allowed to cool. The hydrochloride separating out was purified by recrystallization several times from dilute acid, using animal charcoal each time. The free base was set free by ammonia and recrystallized from dilute alcohol. It melted at 45°. The sulfate was prepared by treating the amine with dilute sulfuric acid. It is slightly soluble in water but soluble in ordinary solvents. The acetyl derivative was prepared by treating the amine with acetyl chloride. It is soluble in alcohol and slightly soluble in water. When recrystallized from alcohol it melted at 110°.

Analyses. Amine hydrochloride for HCl: Calcd. 18.94. Found: 18.67, 18.61.

Amine sulfate for S: Calcd. 7.45. Found: 7.55, 7.37.

Acetyl derivative for N: Calcd. 13.46. Found: 13.18.

Amine Salts of Anthraquinone-1-butyl-thio-ether-5-sulfonic Acid.—The salts of *o*- and *p*-ethylaniline were prepared according to the method of Reid, Mackall and Miller.¹⁷ It was thought that possibly the ethyl group would lower the melting point enough to avoid decomposition and that these might prove good compounds for identification. However, they showed melting points with decomposition similar to the compounds of the toluidine. The following is a comparison with similar compounds prepared from *o*- and *p*-methylaniline.

Methylaniline		Ethylaniline	
<i>ortho</i>	<i>para</i>	<i>ortho</i>	<i>para</i>
234–237°	256–260°	237–239°	247–249°

¹⁷ Reid, Mackall and Miller, *THIS JOURNAL*, 43, 2104 (1921).

Anal. *Ortho* ethyl compound, calcd. for $C_{10}H_{11}O_4NS_2$: S, 12.92. Found: 12.68, 12.86.

Para ethyl compound, calcd. for $C_{10}H_{11}O_4NS_2$: S, 12.92. Found: 13.13, 13.93.

Sulfonation of *p*-Ethylaniline.—Sulfonations of *p*-methylaniline and of *p*-ethylaniline were carried out under the same conditions. Equally good results were obtained with both compounds. In both cases the sulfonic acid group enters the ring *ortho* to the amino group. A mixture of 30 g. of *p*-amino-ethylbenzene and 75 g. of concd. sulfuric acid was kept at 180° until sulfonation was complete. The reaction mixture was poured into 300 g. of water when the free sulfonic acid separated out in the form of white needles. It was recrystallized from water.

In order to determine the position of the sulfonic acid group in the ring, a portion of the acid was diazotized and the diazonium group replaced by a hydrogen atom. By the usual method the sulfonic group was converted into its sulfonamide which, after recrystallization from alcohol, melted at 86°, corresponding to the *m*-ethylsulfonamide described by Semptowski.¹⁸

The helianthine dye prepared by diazotizing this amine and coupling with dimethylaniline resembles very closely helianthine and *p*-methylhelianthine.

Anal. Calcd. for $C_8H_{11}O_2NS$: S, 15.92. Found: 16.17, 15.73.

3-5-Dibromo-4-amino-ethylbenzene.—One equivalent of *p*-ethylaniline hydrochloride dissolved in water was treated with four equivalents of bromine. The solid which separated out was crystallized from alcohol as long, silky, white, thread-like crystals melting at 85°. The corresponding reaction with chlorine yields a pasty mass which could not be purified.

Anal. Calcd. for $C_8H_9Br_2N$: Br, 56.76. Found: 56.32.

Diazo-amino-ethylbenzene.—This compound was prepared by diazotizing aniline and coupling it with *p*-ethylaniline and by the reverse process. The same compound was formed in each case. Aniline (10 g.) was dissolved in a solution of 100 g. of water and concd. hydrochloric acid corresponding to 12 g. of the free acid, and diazotized. This was treated with a solution of 13 g. (0.107 mole) of *p*-ethylaniline in the theoretical amount of acid. A saturated solution of 50 g. of sodium acetate was added with stirring and the reaction mixture allowed to stand for several hours. The compound which separated out was filtered off, pressed on a porous plate and recrystallized from petroleum ether. It crystallized in yellow needles which melted at 75°.

Anal. Calcd. for amino nitrogen: 5.96. Found: 6.16.

***o*-Amino-azo-ethylbenzene.**—We were unable to isolate this compound in the pure state since it forms an oil which cannot be distilled without decomposition and does not solidify at 20°.

***o*-Ethylphenylhydrazine.**—*o*-Ethylphenylhydrazine hydrochloride was prepared by the ordinary methods for the preparation of hydrazines. It was pressed on a porous plate and recrystallized from dilute acid. The free *o*-ethylphenylhydrazine was prepared by warming the hydrochloride with caustic soda solution. It was then extracted with ether. In the free state it is a very unstable liquid, boiling at 156° at 28 mm. and melting at 49–50°. Its hydrochloride forms hydrazones readily. When *p*-tolylaldehyde is treated with an aqueous solution of the hydrochloride, a hydrazone is formed. It decomposes rapidly in the air. After recrystallizing from alcohol, it melted at 102.5–103°.

Anal. Calcd. for $C_8H_{11}N_2.HCl$: HCl, 21.01. Found: 20.81.

***o*-Ethylphenylhydroxylamine.**—Attempts to prepare this compound by all standard

¹⁸ Semptowski, *Ber.*, 22, 2673

methods were unsuccessful. The reduction of *p*-nitro-ethylbenzene with zinc dust in neutral solution does not take place at low temperatures and at a higher temperature the azoxy derivative is formed in small quantities. Zinc dust in alcoholic solution gives a good yield of the azoxy compound. Ammonium sulfide in alcoholic solution has no effect in the cold, while at higher temperatures it gives the amine.

***p*-Ethylazoxybenzene.**—In attempting to prepare the *p*-ethylphenylhydroxylamine by the method used by Bamberger¹⁹ for *p*-methylphenylhydroxylamine, we obtained the *p*-ethylazoxybenzene. This is a striking difference between the behavior of the two nitro compounds.

A water solution of 2.4 g. of calcium chloride was added to a mixture of 28 g. of *p*-nitro-ethylbenzene dissolved in 70 g. of ethyl alcohol. The mixture was boiled under reflux for a half hour during which time 30 g. of zinc dust was added in portions. The zinc oxide was filtered off and the filtrate poured into water. The oil which separated was steam distilled to remove any volatile impurities. When cooled it solidified and was recrystallized from alcohol.

When *p*-ethylazoxybenzene was distilled from iron filings, it gave *p*-ethylazobenzene, which is described by Schultz,²⁰ m. p. 63°.

***p*-Ethylbenzaldehyde.**—We attempted to prepare the *p*-ethylbenzaldehyde from ethylbenzene and carbon monoxide by means of the Gattermann-Koch reaction, using high-speed stirring to accelerate the reaction. Only a trace of the aldehyde was formed.

Azo Dyes from Aniline, *o*- and *p*-Methylaniline and *o*- and *p*-Ethylaniline.—Aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline were diazotized and coupled with Schollkopf's acid and *p*-methylaniline and *p*-ethylaniline with Neville and Winther's acid. Two per cent. dyeings were made on wool skeins, using standard methods for application.

An attempt to isolate the dye from *o*-ethylaniline and Neville and Winther's acid was a failure. The coupling was complete but the solubility of the dye was so great that it could not be salted from solution.

There is a marked change in the color of the dye in going from aniline to methylaniline and a slight deepening in the color in going from methylaniline to ethylaniline. In both the methylaniline and ethylaniline series the *para* dye was deeper in shade than the *ortho*.

The two dyes prepared from *p*-ethylaniline were obtained by recrystallization from alcohol.

Summary

1. An improvement has been made upon the procedure for the preparation of ethylbenzene from benzene and ethylene in the presence of aluminum chloride.

2. The isomeric *o*- and *p*-nitro-ethylbenzenes were separated by one distillation through a high-precision vacuum still, thus eliminating the waste of materials and time necessitated by the older method of fractional distillation.

3. The nitro compounds were reduced to the corresponding amines, and from these amines several new derivatives were prepared.

4. A series of azo dyes was prepared from aniline, *o*- and *p*-methylaniline and *o*- and *p*-ethylaniline to determine the relative effects of the methyl and ethyl groups.

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¹⁹ Bamberger, *Ber.*, 31, 582 (1898)

²⁰ Schultz, *Ber.*, 17, 475 (1884).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

m-DIETHYLBENZENE AND SOME OF ITS DERIVATIVES¹BY J. E. COPENHAVER² AND E. EMMET REID

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Historical

The chemistry of the dimethylbenzenes has been well worked out, while the corresponding ethyl derivatives have been studied to a relatively small extent. The first work upon diethylbenzenes was done by Fittig and König,³ who prepared them from bromobenzene and ethyl chloride by the Fittig synthesis. Aschenbrandt⁴ described the preparation of *p*-diethylbenzene by the Fittig synthesis and from it made several compounds. Anschütz and Immendorf⁵ were the first to prepare the diethylbenzenes by the Friedel and Crafts reaction. They claimed that the *para* isomer was the chief product. Voswinkle⁶ was the first to isolate and critically study the three isomeric diethylbenzenes. He prepared the *meta* and *para* isomers by the Friedel and Crafts reaction. By this procedure he claimed that the *para* compound was the major product and that there was no *ortho* isomer formed.⁷ To prepare the latter he used the Fittig synthesis. He separated the *meta* and *para* isomers by the difference in solubility of the barium salts of the sulfonic acids. He prepared a series of compounds from the sulfonated and nitrated derivatives of each isomer. In the nitration of *m*-diethylbenzene, he did not attempt to separate the nitro isomers, which were undoubtedly formed, and any compound made from his nitro would be a mixture of isomers.

Fournier⁷ used the same method of preparation of the *meta* and *para*-diethylbenzenes as Voswinkle, but instead of the barium salt of the *p*-diethylbenzene sulfonic acid, he used the cadmium salt to purify this isomer, since its barium salt is difficult to crystallize.

The Present Investigation

The ethylbenzenes were prepared by the Friedel and Crafts synthesis by passing ethylene into benzene and aluminum chloride heated to 70–80°, the reaction being accelerated by high speed stirring.⁸

By this procedure there are obtained a series of ethylated benzenes,

¹ Presented at the Philadelphia meeting of the American Chemical Society, September, 1926.

² From the Ph.D. dissertation of J. E. Copenhaver.

³ Fittig and König, *Ann.*, **144**, 284 (1867).

⁴ Aschenbrandt, *Ber.*, **12**, 1303 (1879); *Ann.*, **216**, 211 (1883).

⁵ Anschütz and Immendorf, *Ber.*, **18**, 661 (1885).

⁶ Voswinkle, *Ber.*, **21**, 2829, 3499 (1888); **22**, 315 (1889).

⁷ Fournier, *Bull. soc. chim.*, [3] **7**, 651 (1892).

⁸ (a) Milligan and Reid, *THIS JOURNAL*, **44**, 206 (1922); (b) Milligan and Reid, *Ind. Eng. Chem.*, **15**, 1048 (1923); (c) Berry and Reid, *THIS JOURNAL*, **49**, 3142 (1927).

from the mono- to the hexa-ethylbenzene, the amounts of these formed depending upon the conditions of the experiment and the amount of ethylene introduced. The present investigation was carried out upon *m*-diethylbenzene, which was obtained, along with the *para* isomer and possibly some *ortho*, by the above reaction. The fraction boiling from 180–185° was used, as the boiling points of the three diethylbenzenes as determined by Voswinkle are *ortho*, 184–184.5°; *meta*, 181–182° and *para* 182–183°. The *meta* isomer was considered to be the major constituent of the diethylbenzenes from the above method of preparation of ethylated benzenes and our experiments bear out this relation.

The *m*-diethylbenzene was separated from the isomeric mixture by partial sulfonation and fractional crystallization of the barium salt of the diethylbenzene sulfonic acids. Advantage was taken of the property of *m*-diethylbenzene of being more easily sulfonated than the other two isomers and a process was worked out by which 30% of the isomeric diethylbenzenes could be isolated as the pure *meta* compound. The boiling point of *m*-diethylbenzene was found to be 180.55° (corr).

Another method of separation was investigated but with poor results. It consisted of differential oxidation, followed by partial sulfonation and partial hydrolysis, as was applied to the xylenes by Clarke and Taylor.⁹

When this method was tried with the diethylbenzenes, it was found that, by treatment with dilute nitric acid to oxidize the *ortho* and *para* isomers, nitration instead of oxidation took place. We were unable to identify the nitro product formed but the nitration must have taken place in the side chain, as conditions were more favorable for this than for nitration in the ring.

Another method of separation of the *meta* isomer was experimented with, namely, that of complete sulfonation of the diethylbenzenes using equal volumes of the hydrocarbon and concentrated sulfuric acid, followed by fractional crystallization of the barium salt of the sulfonic acid. As there was a possibility of disulfonation and as the recrystallization of the barium salt is more difficult in the presence of the other sulfonated isomers, this method was abandoned for that of partial sulfonation, as outlined above.

When *m*-diethylbenzene is nitrated with a mixture of concentrated and fuming nitric acid at 30°, a mixture of isomeric mononitro derivatives is obtained. Under the influence of the two ethyl groups, the entering nitro group would be oriented to the 2 or 4 position, with a possibility of some going to the 5 position. Voswinkle prepared a mononitro compound but was uncertain as to the position of the nitro group. He did not attempt to separate the isomers and there is little doubt that he had a mixture of isomers from which he prepared several compounds.

⁹ Clarke and Taylor, *THIS JOURNAL*, 45, 830 (1923).

By passing the nitro product from *m*-diethylbenzene through a high-precision vacuum still¹⁰ we were successful in separating the major isomer from the one or more remaining isomers. This compound constitutes 75% of the total nitro product and is the 4-nitro-*m*-diethylbenzene. Its structure was proved by oxidizing it to the 4-nitro-isophthalic acid by alkaline potassium permanganate. This melted at 245° as given by Huisinga and Holleman.¹¹ 4-Nitro-*m*-diethylbenzene boils at 133° at 4 mm. It is easily reduced to the amine, from which several compounds were made, including a series of azo dyes. The purpose of the preparation of the dyes was to determine the effect upon the color of the ethyl groups as compared with methyl groups in similar dyes.

Experimental

Separation of *m*-Diethylbenzene

To 686 g. (5.12 moles) of the crude diethylbenzenes, boiling from 180–185°, in a two-liter balloon flask, was added 1290 g. (12.5 moles) of concentrated sulfuric acid. The mixture was mechanically stirred at such a rate as to give an emulsion of the hydrocarbon and the acid, the temperature being kept between 15 and 20°. After six hours, when the stirrer was stopped and the mixture allowed to stand for a few minutes, three distinct layers separated. The top layer consisted of the unreacted hydrocarbon; the second, an amber-colored solution, was principally the sulfonated product; and the third, the lowest layer, was almost colorless. It analyzed for approximately 80% of sulfuric acid and contained less than 1% of the sulfonated hydrocarbon. When 300 cc. of water was added, most of it went to the acid layer. After standing for two hours, about half of the lower layer was siphoned off and the remainder, with the two top layers, was transferred to a flask for steam distillation. Steam was passed into the solution and distillation continued until the temperature reached 125° (thermometer in the liquid). This insured complete separation of the unreacted hydrocarbon. There remained in the flask two distinct layers, the top, consisting of the sulfonated hydrocarbon and the lower, the sulfuric acid layer. After cooling, the lower layer was siphoned off, thus freeing the sulfonated hydrocarbon from most of the excess sulfuric acid. The sulfonated hydrocarbon layer was transferred to a three-liter beaker and diluted with 300 cc. of water. A hot, saturated solution of barium hydroxide was added until a slight alkaline reaction to litmus was obtained. It was made again slightly acid with dilute sulfuric acid and then brought to the neutral point with barium carbonate. This procedure avoided the troublesome foaming that results when the carbonate is used exclusively. The solution was diluted to about two and one half liters, boiled and the precipitate filtered off. The barium sulfate cake was washed free of the sulfonated hydrocarbons by boiling with 300–400 cc. of water and filtering. Usually three to four washings were sufficient. The several filtrates were combined and evaporated to about 1500 cc. and then cooled to room temperature. It was found best to stir the solution while it was cooling as this prevented the formation of a hard cake of crystals which, if formed, gave difficulty in filtering. The separation of the pure barium salt of *m*-diethylbenzene sulfonic acid depends upon the fact that this salt is less soluble in water than the barium salts of the other two isomers, as shown by Voswinkle.¹²

¹⁰ Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

¹¹ Huisinga and Holleman, *Rec. trav. chim.*, **27**, 260–286 (1909); *C. A.*, **3**, 420 (1909).

¹² Voswinkle, *Ber.*, **22**, 315 (1889).

The salts of other metals were tried but it was found that the barium salt is the best suited for this separation. The snow-white crystals were placed upon a large Büchner funnel and repeatedly pressed until all of the mother liquor was drawn off. This liquor contained the more soluble barium salts of the *ortho*- and *para*-diethylbenzene sulfonic acids as well as a large quantity of the *meta* isomer. The crystals were dissolved in 300 cc. of water, cooled and filtered as before. Four or five such recrystallizations separated the pure *meta* isomer, as was shown by the melting point of the amide, which was made in the usual way. A second concentration of the combined mother liquors gave a small additional yield of the *meta* isomer. If all of the crystals which came out at room temperature were filtered from the mother liquor, there remained a reddish solution which showed little tendency to crystallize. The barium salt of *m*-diethylbenzene sulfonic acid crystallizes in glistening white plates which are easily soluble in the ordinary solvents. An average run for the separation of the *meta* isomer is as follows: from the 686 g. of the isomeric diethylbenzenes initially used, 292 g. was recovered unreacted, 210 g. (30%) was isolated as the *meta* isomer and the remainder washed into the filtrate. Taking into consideration the large amount of the *meta* isomer isolated and the amount washed into the filtrate to secure the pure fraction, one would be safe in assuming the *meta* isomer to be the major constituent of the isomeric diethylbenzenes.

The amide of *m*-diethylbenzene sulfonic acid crystallizes easily from alcohol and water in long, flat, white needles, forming star-shaped clusters. It melted at 101–101.5°, as given by Voswinkle. The amide of the *ortho* isomer melts at 119° and the *para* at 85°, according to the same author.

The sulfonic acid group was easily removed from the *m*-diethylbenzene sulfonic acid by the method described by Armstrong and Miller.¹³ Equal amounts, by weight, of the barium salt of the sulfonic acid and concentrated sulfuric acid were placed in a balloon flask and steam distilled. The sulfuric acid was diluted with an equal volume of water before it was added to the barium salt. Barium sulfate was precipitated and the benzene sulfonic acid went into solution. Steam was passed into the solution and by external heating of the distillation flask the temperature was increased to 130° (thermometer in the liquid). At about this point the *m*-diethylbenzene sulfonic acid began to hydrolyze, yielding the free hydrocarbon. Then the temperature was gradually increased to 160°, the major portion of the *m*-diethylbenzene coming over between 140 and 150°. Distillation was continued until all of the *m*-diethylbenzene sulfonic acid was hydrolyzed. There was a slight coloration on the remaining acid layer, which showed some decomposition by the acid. From the wide temperature range, it can be readily seen that no narrow temperature limits can be assigned for the hydrolysis of *m*-diethylbenzene sulfonic acid by steam and sulfuric acid. The *m*-diethylbenzene was dried over calcium chloride and distilled. The purity of the compound was indicated by the fact that about 95% of it distilled at one definite temperature, which was 180.55° (corr.). Yield, from the barium salt to the hydrocarbon, 95–97%. The physical properties of *m*-diethylbenzene resemble very closely those of the xylenes, it being a colorless, very mobile liquid with a pleasant, sweetish odor; $d_4^{20} = 0.8798$; $d_{25}^{20} = 0.8597$; $n_D^{25} = 1.4926$; $n_D^{20} = 1.4955$; $n_D^{15} = 1.4778$; $n_D^{10} = 1.4998$.

4-Nitro-*m*-diethylbenzene.—To obtain the formation of only the mononitro derivative of *m*-diethylbenzene, a number of experiments were made to determine the optimum temperature and concentration of nitric acid to give approximately 50% nitration, which would minimize the formation of higher nitro products. Sulfuric acid could not be used to take up the water formed in the reaction as *m*-diethylbenzene sulfonates easily, even at low temperatures. The following method was found to be very satisfactory. A mixture of 60 g. of concd. nitric acid (sp. gr. 1.42) and 40 g. of fuming

¹³ Armstrong and Miller, *J. Chem. Soc.*, 45, 148 (1884).

nitric acid (sp. gr. 1.49–1.50) was used for each 100 g. of *m*-diethylbenzene. The acid was added slowly to the hydrocarbon while the mixture was well stirred and the temperature kept below 30°. The mixture was stirred at 30° for one and one-half hours after all of the acid was in and then diluted with 100 cc. of water. The oil layer was removed and washed with water and with a 10% sodium hydroxide solution to remove any phenols. After washing it free of the alkali, it was diluted with a small amount of ether, dried over calcium chloride and distilled. After removing the unreacted *m*-diethylbenzene, it was found that the nitro product distilled over a range of 105–138° at 5 mm. pressure, which strongly indicated a mixture of isomeric mononitro derivatives. A small residue in the distilling flask showed the formation of some of the higher nitro compounds.

In order to secure a separation of these nitro isomers, a high-precision fractional vacuum still was built as described by Peters and Baker,¹⁰ with slight changes to suit our needs. The inner column was sealed directly to the distilling flask and was one continuous piece throughout the apparatus. This column was 225 cm. long and 25 mm. in diameter. No pre-air heater was used and the distillate receiver was arranged so that the measured distillate could be removed without breaking the vacuum on the whole system. By running the mixture of isomers through this still, reading every minute the temperature of the distillate and the volume distilled, the points at which cuts should be made were clearly indicated when these data were plotted. After determining these points the isomers could be sharply separated by redistillation. The lower-boiling isomers distilled between 107 and 120° at 4 mm. pressure, there being no marked temperature break within that range. From 120° the temperature rose sharply to 133°, pressure constant, and remained at that point throughout the distillation. This isomer composed 75% of the mixture and was the 4-nitro-*m*-diethylbenzene. The structure was definitely proved by oxidizing it to 4-nitro-isophthalic acid, which melted at 245°. From the boiling point data, the low-boiling fraction seemed to consist of two possible isomers, namely, 2-nitro-*m*-diethylbenzene and 5-nitro-*m*-diethylbenzene. As there was only a small quantity of this mixture, no further study of it was made. Voswinkle gave 280–285°, with decomposition, as the boiling point of the mononitro derivative which he prepared. The nitro derivatives are amber-colored (reddening upon standing for several months), pleasant-smelling liquids. 4-Nitro-*m*-diethylbenzene boils at 133° at 4 mm.; $d_4^{25} = 1.0860$; $d_{25}^{25} = 1.0644$; $n_D^{25} = 1.5300$.

4-Amino-*m*-diethylbenzene.—The 4-nitro-*m*-diethylbenzene was easily and completely reduced to the amine by iron filings and acetic acid. The reaction was complete in about six hours when the mixture was heated on a boiling water-bath. The solution was made alkaline, the amine steam distilled, dried over calcium chloride and distilled under reduced pressure. The freshly distilled amine was almost colorless but gradually assumed a reddish color upon standing. It is insoluble in water, soluble in ether, alcohol, etc. The amine hydrochloride formed very easily and crystallized in long, clustered, anhydrous needles which are very soluble in water. Voswinkle prepared the acetyl derivative and gave 194° as its melting point. We prepared the same derivative and found that it crystallizes in long, flat, anhydrous, white needles that melt at 112–113.5°, (corr.). The benzoyl derivative crystallizes in white, anhydrous, lustrous plates which melt at 176.5° (corr.). The boiling point of the amine is 116.5° (corr.) at 12 mm. and 141° (corr.) at 30 mm. pressure; $d_4^{25} = 0.9651$; $d_{25}^{25} = 0.9545$; $n_D^{25} = 1.5395$.

Anal. Calcd. for $C_{10}H_{14}N$: N, 9.40. Found: 9.44.

4-Hydroxy-*m*-diethylbenzene.—This phenol was prepared by heating the diazo-tized amine and steam distilling the product. It was washed with 50% sulfuric acid, dried over potassium carbonate and distilled in a vacuum; yield, 78%. An attempt was made to prepare the phenol from the sodium salt of *m*-diethylbenzene sulfonic acid

but with little success. It is an amber-colored liquid, completely soluble in sodium hydroxide solution, very slightly soluble in water and soluble in ordinary organic solvents. It has a distinct phenolic odor. It gave no color with aqueous ferric chloride but with an alcohol-water solution it gave a green coloration. 4-Hydroxy-*m*-diethylbenzene boils at 124.5–125.5° (corr.); $d_4^{20} = 0.9986$; $d_{25}^{25} = 0.9794$; $n_D^{25} = 1.5218$.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.40. Found: C, 79.79; H, 9.73.

4-Chloro-*m*-diethylbenzene.—This compound was prepared from the amine by the Sandmeyer reaction, using the procedure outlined by Marvel and McElvain for the preparation of the chlorotoluenes.¹⁴

The amine was diazotized and added to the freshly prepared cuprous chloride solution at 0°. After stirring for two hours, the brown addition product was decomposed by gradually heating, and the chlorine compound steam distilled. It was washed with sodium hydroxide and sulfuric acid, dried and distilled in a vacuum; yield, 50%. Istiate¹⁵ prepared the chloro derivatives of the diethylbenzenes from monochlorobenzene, ethylene and aluminum chloride, but did not attempt to separate the different chloro isomers. The 4-chloro-*m*-diethylbenzene is a colorless, pleasant-smelling liquid boiling at 94.5° (corr.) at 12 mm.; $d_4^{20} = 1.0335$; $d_{25}^{25} = 1.0119$; $n_D^{25} = 1.5149$.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.04. Found: 20.66.

4-Bromo-*m*-diethylbenzene.—The bromine derivative was prepared by the Sandmeyer reaction by adding the diazotized amine to the cuprous bromide-hydrobromic acid mixture at 0–5° and also at 105°. The yield at both of these temperatures was very poor but the low-temperature reaction gave the best yield, it being about 19%. Voswinkle prepared the monobromo derivative by direct bromination but here again he was uncertain as to the position of the bromine atom. The purification of this halide was similar to that for the chlorine compound. It is a colorless liquid boiling at 106.5° (corr.) at 12 mm.; $d_4^{20} = 1.2709$; $d_{25}^{25} = 1.2462$; $n_D^{25} = 1.5359$.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.52. Found: 38.55.

4-Iodo-*m*-diethylbenzene.—This compound was prepared by the usual method of adding potassium iodide to the diazotized amine. It was purified by the method given under the chloro derivative. It is a colorless liquid boiling at 131.5° (corr.) at 12 mm.; $d_4^{20} = 1.5026$; $d_{25}^{25} = 1.4740$; $n_D^{25} = 1.5729$.

Anal. Calcd. for $C_{10}H_{13}I$: I, 48.81. Found: 47.16.

***m*-Diethylbenzene Iodoso Chloride.**—This compound was prepared by treating 4-iodo-*m*-diethylbenzene, dissolved in carbon tetrachloride, with chlorine at 0°. The iodoso chloride is very soluble in this solvent and separated out in yellow crystals as the latter evaporated. This compound was quite unstable, even at low temperatures, and decomposed, giving off free chlorine. The freshly prepared crystals melted with decomposition at 51–53°. Attempts to prepare the iodoso oxide were unsuccessful.

4-Cyano-*m*-diethylbenzene.—This nitrile was prepared from the amine by the Sandmeyer reaction.¹⁶ The neutralized diazonium chloride was added to the cuprous cyanide solution at 0–5° and the diazonium complex decomposed by heating, the nitrile being purified in the usual way. It is a yellowish liquid boiling at 134° (corr.) at 12 mm.; $d_4^{20} = 0.9699$; $d_{25}^{25} = 0.9507$; $n_D^{25} = 1.5195$.

Anal. Calcd. for $C_{11}H_{13}N$: N, 8.80. Found: 8.45.

¹⁴ Marvel and McElvain, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33; *C. A.*, 20, 173 (1926).

¹⁵ Istiate, *Ann. chim. phys.*, [6] 6, 413 (1885).

¹⁶ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 69; *C. A.*, 20, 181 (1926).

***m*-Diethylthiocarbanilide.**—This derivative was prepared by the method given by Snedker,¹⁷ which consisted of using one molal proportion of the amine to 1.25 moles of carbon bisulfide and cooling to about 10°. While the solution was being stirred a 40% solution of sodium hydroxide was added. After stirring for a few minutes, the carbon bisulfide was allowed to evaporate. The *m*-diethylthiocarbanilide crystallized in very fine, white needles which, when recrystallized from alcohol and water, melted at 144.5° (corr.); yield, 36.5%.

Anal. Calcd. for C₂₁H₂₃N₂S: S, 9.42. Found: 9.39.

Comparison of Azo Dyes Prepared from Aniline, 4-Amino-*m*-Dimethylbenzene and 4-Amino-*m*-Diethylbenzene

In order to see what effect the ethyl groups of 4-amino-*m*-diethylbenzene would have upon the color of dyes prepared from it, in comparison with those obtained from 4-amino-*m*-diethylbenzene and aniline, a series of dyes was made from these amines. They were diazotized and each coupled with R-salt, chromotrope, H-acid, etc., as second components. The dyes were made and applied to the wool without isolation from solution. The procedure for the three amines and ten second components is as follows.

One-hundredth of a mole of each amine was diazotized in the usual way and the solution diluted to 100 cc. One-thousandth of a mole of each of the ten second components was placed in a beaker and to each was added 50 cc. of water and 2.5 cc. of a 10% sodium carbonate solution. After obtaining complete solution of the naphthalene salt, the solution was cooled to 5° and 10 cc. of the cold diazotized amine solution was added, with stirring. The coupling was usually very rapid and in most cases the dye was in complete solution. The dye solution was kept cold for about an hour and then allowed to come to room temperature. Each dye solution was diluted to 100 cc. and 50 cc. of this solution was used for each dyeing. The 50 cc. of dye solution taken was diluted to 200 cc. and 10 cc. of 5% sulfuric acid added. The entering of the skeins, etc., was carried out as is usual for wool dyeings. The dye-bath was heated until complete exhaustion of the dye by the wool, which required from thirty to sixty minutes. By the above procedure the amount of dye on the wool varied from one component to the other but the amount formed from the three amines with any one second component was practically the same.

Table I is a classification of the dyes from the three amines. The introduction of the methyl groups in the molecule has a very pronounced effect, giving a change in color as would be expected. In comparing the methyl and ethyl groups, there is little change in the color but the intensity of the color is increased in a majority of the comparative dyeings, namely, nos. 1, 2, 4, 6, 7 and 9, and in 5 and 10 the intensity is the same. In numbers 3 and 8, the reverse is true but this is possibly due to incomplete coupling.

¹⁷ Snedker, *J. Soc. Chem. Ind.*, **44**, 486T (1925).

Taking the series as a whole, we can definitely say that the presence of the ethyl groups in the amine molecule gives a decided effect over the methyl groups in the intensity of the color of the dye.¹⁸

TABLE I

CLASSIFICATION OF AZO DYES MADE FROM ANILINE, *m*-DIMETHYLANILINE AND *m*-DIETHYLANILINE BY COUPLING WITH NAPHTHALENE DERIVATIVES

Second component	Aniline	<i>m</i> -Dimethylaniline	<i>m</i> -Diethylaniline
1. H-acid	Bordeau	Bordeau	Deeper Bordeaux
2. Chromotrope	Red	Crimson	Deeper crimson
3. Armstrong's acid	Yellow	Dull yellow	Yellow
4. Schaeffer's salt	Orange	Scarlet	Deeper scarlet
5. R-salt	Deep orange	Red	Red
6. J-acid	Yellow-brown	Red-brown	Deeper red-brown
7. <i>p</i> -Aminobenzoyl-J-acid	Burnt orange	Red	Deeper red
8. J-acid urea	Orange	Red	Lighter red
9. <i>p</i> -Aminobenzoyl- <i>p</i> -amino-benzoyl-J-acid	Orange	Red	Deeper red
10. Neville and Winther's acid	Deep orange	Red	Red

Summary

1. *m*-Diethylbenzene has been separated from its isomers by partial sulfonation and fractional crystallization of the barium salt of the sulfonic acid.

2. 4-Nitro-*m*-diethylbenzene has been separated from its isomers and reduced to the amine, from which several derivatives were made by standard methods.

3. A series of azo dyes was made from aniline, *m*-diethylbenzene and *m*-diethylbenzene to determine the influence of the ethyl groups over the methyl groups in the color of the dyes. It was found that the colors were the same but the intensity of the color was increased.

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¹⁸ The authors wish to thank the Jackson Laboratory and the Technical Laboratory of E. I. du Pont de Nemours and Co. for advice in the preparation of the dyes, for furnishing the second components and for classifying the dyeings.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NEBRASKA]

DICARBOXYPHENYLARSONIC ACIDS. II
3,4-DICARBOXYPHENYLARSONIC ACID AND SOME OF ITS
DERIVATIVES

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Previous to this time, only three dicarboxyphenylarsonic acids have been prepared. Isophthalarsonic acid, or 2,4-dicarboxyphenylarsonic acid, was prepared by Michaelis from 2,4-dimethylphenylarsonic acid by oxidation with potassium permanganate in alkaline solution.¹ According to the German patents, 4-acetyl-amino-2,5-dicarboxyphenylarsonic acid was prepared by oxidation of 4-acetyl-amino-5-carboxy-2-methylphenylarsonic acid with potassium permanganate in alkaline solution.² 2,3-Dicarboxyphenylarsonic acid, the first dicarboxyphenylarsonic acid with the carboxyl groups ortho to each other, was prepared by Hamilton and Frazier³ by first nitrating *o*-phthalic acid, then reducing the nitro compound to 3-amino-*o*-phthalic acid and finally introducing the arsonic acid group by means of Bart's reaction.⁴

As a further contribution to the study of dicarboxyphenylarsonic acids, 3,4-dicarboxyphenylarsonic acid and some of its derivatives have been prepared. This is the first dicarboxyphenylarsonic acid to be obtained by the introduction of the arsonic group into the neutral ester of an aromatic dicarboxy acid. 4-Nitro-*o*-phthalic acid was first obtained by preparing phthalimide from phthalic anhydride and urea, reducing phthalimide to phthalide, nitrating phthalide and oxidizing 5-nitrophthalide to 4-nitro-*o*-phthalic acid. On direct reduction of 4-nitro-*o*-phthalic acid with tin and hydrochloric acid, Bogert⁵ and Miller⁶ found that carbon dioxide was evolved, forming *m*-aminobenzoic acid. Thus to prepare 4-amino-*o*-phthalic acid, it was necessary to esterify 4-nitro-*o*-phthalic acid before reduction in order to protect the carboxyl groups. The dimethyl-4-nitrophthalate was then reduced with zinc dust and hydrochloric acid in the presence of alcohol.

The arsonic acid group was introduced directly into dimethyl-4-amino-phthalate following the method used by Bart to prepare 2-carboxyphenylarsonic acid.^{4b} Bart observed that substitution of the arsonic acid group did not occur when benzene diazonium chloride was treated with arsenious acid in weakly or strongly acid solution, the diazo compound

¹ Michaelis, *Ann.*, 320, 335 (1902).² Farbwerke vorm. Meister, Lucius and Bruning, Ger. pat. 203,717 (1907).³ Hamilton and Frazier, *THIS JOURNAL*, 48, 2414 (1926).⁴ (a) Bart, Ger. pat. 250,264 (1910); (b) *Ann.*, 429, 55 (1922).⁵ Bogert and Renshaw, *THIS JOURNAL*, 30, 1136 (1908).⁶ Miller, *Ber.*, 11, 992 (1878); *Ann.*, 208, 223 (1881).

behaving exactly the same as if arsenious acid were not present. The diazonium compound gave off nitrogen, gradually changing to phenol. However, when the reaction was carried out in the presence of hydroxyl ion of not too high concentration, the diazo compound reacted with the arsenious acid to form phenylarsonic acid. The failure to form the arsonic acid after treatment of the diazonium chloride with arsenious acid in the presence of hydrogen ion, led Bart to conclude that the diazonium group could not be replaced by the arsonic acid radical. Because of the favorable effect of hydroxyl ion on the formation of arsonic acids, Bart concluded that the reaction took place only after the transformation of the diazonium to the diazohydrate form, which is stable only in alkaline solution. Further investigation by Bart showed that hydroxyl ion in high concentration had a negative influence on the course of arsonic acid formation. It was not known whether this phenomenon depended on the fact that the diazotate, which is formed by increasing the hydroxyl-ion concentration, had a lower tendency to react with arsenious acid, or whether the activity of arsenious acid as a reducing agent was decreased. It was certain, according to Bart, that the best reaction took place when the hydroxyl-ion concentration was just sufficient for the formation of the *syn*-diazohydrate from the diazonium compound.

Bart also found that if the diazo compound contained a strongly negative group such as nitro or carboxyl, a good reaction with arsenious acid occurred even with a small hydroxyl-ion concentration, due to the great tendency of such diazonium compounds to form the diazohydrate. If the negative group was meta or para to the arsonic acid group, a somewhat stronger alkalinity was found to be necessary than for a compound containing the negative group in the ortho position. This was thought to be due, probably, to the further distance of the negative group from the diazonium group, a slightly higher alkalinity being required to form the *syn*-diazo compound.

Thus, in preparing the dimethyl ester of 3,4-dicarboxyphenylarsonic acid, the diazonium mixture, before being added to the sodium arsenite solution, was just neutralized with sodium hydroxide solution in order to form the *syn*-diazohydrate. This change was apparent, for just at the neutral point an orange precipitate separated from the clear diazonium solution. Because of the presence of the negative carboxyl groups, a very low hydroxyl-ion concentration was used. The diazonium solution was just neutralized with sodium hydroxide solution, but none was added to the sodium arsenite solution, a sufficient hydroxyl-ion concentration resulting from the hydrolysis of the sodium arsenate. The neutral methyl ester of 3,4-dicarboxyphenylarsonic acid was hydrolyzed with metallic sodium and alcohol, forming the sodium salt, which was converted into the silver salt. From the silver salt pure 3,4-dicarboxyphenylarsonic acid was obtained

Experimental Part

Preparation of Phthalimide.—The phthalimide used in the synthesis of 3,4-dicarboxyphenylarsonic acid was prepared according to the method of Herzog;⁷ yield 97%.

Preparation of Phthalide.—Phthalide was prepared readily by the method of Reissert.⁸ The yield from 1130 g. of phthalimide was 743 g. of phthalide (73%); m. p. 71–73°.

Nitration of Phthalide.—Hoenig nitrated phthalide with potassium nitrate and concd. nitric acid and believed that the product was 4-nitrophthalide.⁹ Teppema showed that Hoenig's product was 5-nitrophthalide instead of the 4-nitro derivative.¹⁰ 5-Nitrophthalide was prepared very satisfactorily by the method of Hoenig. From 743 g. of phthalide, 704 g. of crude 5-nitrophthalide was obtained. On recrystallization from ethyl alcohol, the nitrophthalide melted at 132–134°.

Oxidation of 5-Nitro-phthalide.—By following the method of Bogert and Boroschek,¹¹ 90% yields of 4-nitro-*o*-phthalic acid melting at 162–163° were obtained.

Preparation of the Dimethyl Ester of 4-Nitro-*o*-phthalic Acid.—Dimethyl-4-nitrophthalate was prepared by the method of Bogert and Renshaw,¹² which involved the sulfuric acid method of esterification. Four hundred g. of pure 4-nitro-*o*-phthalic acid yielded 448 g. of the ester melting at 69–71°; yield, 86%.

Reduction of Dimethyl-4-nitrophthalate to Dimethyl-4-aminophthalate.—Dimethyl-4-nitrophthalate was reduced with alcoholic hydrochloric acid and zinc dust according to the method of Bogert and Renshaw.¹³ Tan-colored, glistening plates of dimethyl-4-aminophthalate melting at 80–84° were obtained in 75% yield.

Arsonation of Dimethyl-4-aminophthalate.—The method which was used by Bart¹⁴ to prepare 2-carboxyphenylarsonic acid was modified and employed in the arsonation of dimethyl-4-aminophthalate. Sixty-two g. of dimethyl-4-aminophthalate was dissolved in a three-liter beaker containing 1200 cc. of water and 105 cc. of hydrochloric acid (sp. gr. 1.18). The beaker was surrounded by a freezing mixture and the solution was cooled below 0° by the aid of a motor-driven stirrer. With constant stirring and keeping the temperature below 0°, a solution of 24 g. of sodium nitrite in 300 cc. of water was added drop by drop by means of a separatory funnel until starch iodide paper indicated an excess of nitrous acid. After stirring for fifteen minutes, the excess hydrochloric acid was carefully neutralized with sodium hydroxide solution, care being taken to keep the temperature below 0°. At the neutral point, as indicated by Congo Red paper, an orange precipitate separated. The diazo mixture, kept at 0°, was added slowly with constant stirring to a three-gallon crock containing a solution of 1500 cc. of water, 150 g. of sodium arsenite, and 15 g. of copper sulfate. The purpose of the copper sulfate was to serve as a catalyst. After each addition of the diazo mixture, nitrogen was evolved. A red coloration, spoken of by Bart,¹⁴ when the diazo solution was first poured into the sodium arsenite solution, was not noticed. Since a good yield of the arsonated product was obtained, this indicated that the red coloration was not necessary for a good reaction. After the diazo solution had all been added, the mixture was stirred for one hour. The resulting brown material was then heated to insure com-

⁷ Herzog, *Z. angew. Chem.*, **32**, 301 (1919).

⁸ Reissert, *Ber.*, **46**, 1489 (1913).

⁹ Hoenig, *Ber.*, **18**, 3447 (1885).

¹⁰ Teppema, *Rec. trav. chim.*, **42**, 30 (1925).

¹¹ Bogert and Boroschek, *This Journal*, **23**, 753 (1901).

¹² Bogert and Renshaw, *ibid.*, **24**, 618 (1906).

¹³ *Ref. 4b*, p. 86.

¹⁴ *Ref. 4b*, p. 61.

plete removal of nitrogen, filtered, acidified with hydrochloric acid to Congo Red paper and evaporated to dryness. The last stages of the evaporation were carried out over a water-bath and finally in an oven at 150°. The yellow residue was pulverized and extracted at room temperature with 400 cc. of absolute methyl alcohol, filtered and the residue washed with methyl alcohol. The yellow filtrate and the washings were combined and distilled to remove most of the methyl alcohol. The residue in the distilling flask was poured into an evaporating dish and heated over a water-bath. The methyl ester of 3,4-dicarboxyphenylarsonic acid remained as a sticky, yellow-brown substance. On drying overnight in an oven at 140° the sticky compound changed to a yellow, crystalline material; yield, 77–80%.

Hydrolysis of the Dimethyl Ester of 3,4-Dicarboxyphenylarsonic Acid.—Fifty g. of the crude dimethyl ester of 3,4-dicarboxyphenylarsonic acid was dissolved in 300 cc. of absolute ethyl alcohol. Alcohol which was free from water was used in order to obtain the sodium salt as a solid rather than as an oil. Some of the salt and arsenic trioxide present in the crude ester did not dissolve and were removed by filtration. When a solution of 25 g. of metallic sodium in 400 cc. of ethyl alcohol was added, the cream-colored sodium salt precipitated immediately. The mixture was refluxed for one hour. Excess sodium was used to prevent the product from darkening and becoming sticky. The sodium salt was filtered, washed with ethyl alcohol and dried overnight at 140°. The yield was quantitative.

Preparation of the Silver Salt of 3,4-Dicarboxyphenylarsonic Acid.—Fifty-nine grams of the sodium salt of 3,4-dicarboxyphenylarsonic acid was dissolved in 100 cc. of water, forming a very viscous, brown solution. The solution was slightly acidified with nitric acid and upon the addition of a solution containing 108 g. of silver nitrate in 100 cc. of water, the silver salt precipitated.

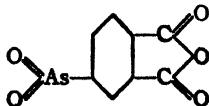
Preparation of 3,4-Dicarboxyphenylarsonic Acid.—The silver salt was filtered, washed with water and, while still wet, was suspended in 300 cc. of water. Conc'd. hydrochloric acid was added until the heavy, curdy precipitate of silver chloride was completely formed. On filtering off the silver chloride, a yellow filtrate was obtained which contained 3,4-dicarboxyphenylarsonic acid in solution. The filtrate was decolorized with charcoal and the silver salt reprecipitated on the addition of a solution of 100 g. of silver nitrate in 100 cc. of water. The white silver salt was filtered, suspended in water, acidified with hydrochloric acid and the silver chloride removed by filtration. On evaporation of the filtrate and drying in an oven at 80°, pure 3,4-dicarboxyphenylarsonic acid remained as a light yellow, crystalline mass; yield 40%, calculated on the basis of the sodium salt.

3,4-Dicarboxyphenylarsonic acid melts and effervesces at 180°. Clusters of light yellow crystals are obtained from a very concentrated solution of 3,4-dicarboxyphenylarsonic acid. It is highly soluble in hot or cold water and in methyl alcohol and insoluble in ether, benzene and chloroform.

Anal. Sample dried at 80°, subs., 0.1891: 24.50 cc. of 0.05312 *N* iodine solution. Calcd. for $C_6H_4O_7As$: As, 25.85. Found: 25.81.

Derivatives

The Anhydride.—The anhydride of 3,4-dicarboxyphenylarsonic acid was prepared by heating the free acid for three days at 160° under reduced pressure in the presence of phosphorus pentoxide. Water splits off from the carboxyl groups and the arsonic acid group, forming the following compound



The anhydride condensed with phenol and resorcinol, forming compounds similar to phenolphthalein and fluorescein.

Anal. Subs., 0.1016, 0.0904: 15.90, 14.30 cc. of 0.04986 *N* iodine solution. Calcd. for $C_8H_5O_4As$: As, 29.51. Found: 29.26, 29.58.

The Methyl Ester.—The methyl ester of 3,4-dicarboxyphenylarsonic acid is a light yellow, crystalline solid which is readily soluble in water, ether, benzene, chloroform, methyl alcohol and ethyl alcohol.

Anal. Subs., 0.5272, 0.2725: 68.00, 34.47 cc. of 0.04933 *N* iodine solution. Calcd. for $C_{10}H_{11}O_7As$: As, 23.57. Found: 23.86, 23.40.

The Ethyl Ester.—The ethyl ester of 3,4-dicarboxyphenylarsonic acid was prepared by refluxing the free acid with absolute ethyl alcohol for fourteen hours. On evaporation of the alcohol and drying in a vacuum oven at 80°, a yellow, sticky material remained which solidified on cooling. The ethyl ester of 3,4-dicarboxyphenylarsonic acid readily absorbs moisture and is soluble in water, methyl alcohol, ether and carbon tetrachloride.

Anal. Subs., 0.2703, 0.1739: 32.20, 20.75 cc. of 0.04845 *N* iodine solution. Calcd. for $C_{12}H_{13}O_7As$: As, 21.66. Found: 21.64, 21.68.

The Neutral Trisodium Salt.—The neutral trisodium salt of 3,4-dicarboxyphenylarsonic acid is a cream-colored solid very soluble in water, and insoluble in methyl alcohol, ether, benzene and chloroform.

Anal. Subs., 0.1346, 0.1122: 14.50, 12.30 cc. of 0.05312, 0.04986 *N* iodine solution. Calcd. for $C_8H_4O_7AsNa_3$: As, 21.05. Found: 21.45, 20.50.

The Tetrasodium Salt.—The tetrasodium salt of 3,4-dicarboxyphenylarsonic acid is a cream-colored solid very soluble in water and insoluble in methyl alcohol, ether, benzene and chloroform.

Anal. Subs., 0.0947, 0.1050: 9.8, 11.07 cc. of 0.04986 *N* iodine solution. Calcd. for $C_8H_3O_7AsNa_4$: As, 19.83. Found: 19.35, 19.72.

The Silver Salt.—The silver salt of 3,4-dicarboxyphenylarsonic acid is a white solid, insoluble in water, methyl alcohol, ether, benzene and chloroform.

Anal. Subs., 0.1272, 0.7251: 0.1001, 0.5671 g. of AgCl. Calcd. for $C_8H_3O_7AsAg_4$: Ag, 60.14. Found: 59.22, 58.86.

Summary

1. 3,4-Dicarboxyphenylarsonic acid has been prepared and its properties have been studied.

2. The anhydride, methyl ester, ethyl ester, trisodium salt, tetrasodium salt and the silver salt of 3,4-dicarboxyphenylarsonic acid have been prepared and their properties determined.

3. Derivatives of the anhydride are being studied.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CARBOHYDRATE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

OPTICAL ROTATION AND ATOMIC DIMENSION. VII. THE HALOGENO-HEPTA-ACETYL DERIVATIVES OF GENTIOBIOSE

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In the sixth article of this series, it was reported that the specific rotational values of the halogen hepta-acetyl derivatives of two bioses (cellobiose and glucosido-mannose) deviate from the regular relationship observed for the monose sugars and further that an agreement is obtained by excluding the values for the fluoro derivatives. This conclusion was also supported by the values for the chloro, bromo and iodo compounds of lactose measured by Hudson and Kunz¹ (the fluoro derivative being amorphous). These three bioses possess the same type of carbon attachment in their structural formulas, the two constituent monoses being attached to each other by an oxygen atom in the same way (according to the latest views the *fourth* carbon of the one monose to the *first* carbon of the second).

The preparation and the rotational values of the pure crystalline fluoro, chloro, bromo and iodo derivatives of acetylated gentiobiose are described in the present article. The synthesis of this biose by Helferich and co-workers² leaves hardly any doubt that in gentiobiose the *sixth* carbon of the one monose is attached through an oxygen atom to the *first* carbon atom of the other. Gentiobiose is, therefore, a representative of the so-called "straight chain" bioses, the others being representative of the branched chain bioses. The data for the specific rotations compiled in Tables I and II show that both kinds of bioses behave in the same

TABLE I

COMPARISON OF SPECIFIC ROTATIONS OF BIOSE DERIVATIVES WITH REPRESENTATIVE MONOSE DERIVATIVES (INCLUDING FLUORO DERIVATIVES)

	Gentio- biose	Derivatives of Cello- biose	Glucosido- mannose	Respective spec. rot. diff.			Respective spec. rot. diff. reduced			Specific rot. diff. of monose sugars (glucose) re- duced to Bragg's atomic diameter difference
F	+ 43.8	+ 30.6	+ 13.6	36.7	41.1	37.6	41	41	41	41
Cl	+ 80.5	+ 71.7	+ 51.2	20.6	24.1	26.7	23	24	29	17
Br	+101.1	+ 95.8	+ 77.9	25.0	29.9	33.6	28	30	37	21
I	+126.1	+125.7	+111.5							

¹ Hudson and Kunz, *THIS JOURNAL*, **47**, 2052 (1925).

² (a) Helferich and others, *Ann.*, **447**, 27 (1926); (b) **450**, 219⁷(1926).

TABLE II

COMPARISON OF SPECIFIC ROTATIONS OF BIOSE DERIVATIVES WITH REPRESENTATIVE MONOSE DERIVATIVES (EXCLUDING FLUORO DERIVATIVES)

	Gentio- biose	Derivatives of Cello- biose	Lactose	Glucosido- mannose	Respective spec. rot. diff.	Respective spec. rot. diff. reduced	Spec. rot. diff. of monose suga. (glucose) redu. to Bragg's atom diameter diff.
Cl	+ 80.5	+ 71.7	+ 83.9	+ 51.2	20.6 24.1 24.8 26.7	17 17 17 17	17
Br	+101.1	+ 95.8	+108.7	+ 77.9	25.0 29.9 28.2 33.6	21 21 20 21	21
I	+126.1	+125.7	+136.9	+111.5			

manner: by including the fluoro derivatives a deviation from the regular relationship of the monose sugars is observed, whereas by excluding the fluoro derivatives the *same ratio 17:21* is found again. The ratio 41:17:21 obtained from the specific rotational values of the halogen derivatives of the monose sugars agrees closely with the ratio derived from the calculations of de Boer and van Arkel³ for distances of the carbon atom to the halogen atoms in carbon compounds. This ratio is 41:17:22.6.

The interpretation stated and discussed in the preceding article⁴ holds also for the gentiobiose derivatives. Besides α -fluoro-, chloro-, bromo- and iodo-hepta-acetylgentiobiose impure β compounds of chloro- and iodo-hepta-acetylgentiobiose can be obtained. Starting from β -octa-acetylgentiobiose in acetic anhydride solution, which is saturated at -15° with hydrochloric acid, the β -chloro derivative is first formed and subsequently converted to the α -chloro compound. On account of this conversion, which is much enhanced by zinc chloride (see experimental part for further information) and which even takes place in a pure chloro-form solution, a mixture in which the β compound predominated is not easily obtained.⁵

³ De Boer and van Arkel, *Z. Physik*, **41**, 27 (1927). Also their value for the distance carbon-hydrogen agrees with the respective rotational differences of the salicin derivatives reported in Part V.

⁴ That as a result of the complicated structure of the molecule other atoms are situated in the neighborhood of the halogen atoms, whereby these halogen atoms are selectively influenced.

⁵ The observed facts may be studied further for the purpose of obtaining more detailed information on the mechanism of substitution. An interesting treatment of this subject is given by Hückel ["Konfigurationsänderungen bei Substitutionsreaktionen," *Z. angew. Chem.*, **39**, 842 (1926)]. The positions of α - and β -hydroxyl, acetyl and halogen in the molecule having been established and correlated, and the nomenclature having therefore been put on a sound basis [Hudson, *THIS JOURNAL*, **46**, 463 (1924); Böseken, *Ber.*, **46**, 2612 (1913); Pictet, *Helv. Chim. Act.*, **3**, 649 (1920)], the conclusion may be reached that the *Walden inversion* from β -octa-acetyl gentiobiose to

Experimental Part

General Remarks.—For all determinations of the specific rotation U. S. P. chloroform or purified chloroform was used. The volume of the solution was made up in the same flask to 24.9767 cc. at 20°, which must be multiplied by the factor 4.0038 to obtain 100 cc. The reading was made in the same 4dm. tube at 20° and is given in circular degrees.

β -Octa-acetylgentiobiose.—The preparation by Hudson and Johnson⁶ was improved, yielding a method similar to the method of Haworth and Wylam.⁷ After the method had been tested with small quantities it was found that 4 kg. of powdered gentian root could be worked up at one time. The weevils that infest the root and powder may in some cases reduce the yield to *nil*. A genuine powder yielded originally about 3% of pure octa-acetylgentiobiose, of which 1 kg. was prepared. The remaining powder was kept in tin containers. After one year only about 0.5% yield could be obtained from this powder, and a few months later none was obtained.

Four kilograms of powdered gentian root was mixed with 35 liters of water in a 16-gallon crock; 8 small cakes of bakers' yeast was added and the mixture was allowed to ferment to completion, which required two days, an additional 8 cakes of yeast having been added on the morning of the second day. The mixture was stirred occasionally with a paddle. Lead subacetate solution (1600 cc. of specific gravity 1.25) was added and the mixture was well stirred and filtered on large Büchner funnels and washed with a few liters of water. The filtrate was treated with hydrogen sulfide until all of the lead was precipitated. The excess hydrogen sulfide was blown out with a current of air. The liquid was then filtered on Büchner filters containing a layer of hot decolorizing carbon (heated in a pan with boiling water). The almost colorless filtrate was evaporated in a large distilling apparatus in a vacuum to a sirup of high density, the maximum temperature of the outside bath being 65°. When the gentian powder has undergone deterioration the filtrate is more acid and should be neutralized with sodium bicarbonate.

The sirup was digested under a reflux condenser on a steam-bath with 1200 cc. of absolute methyl alcohol with frequent, vigorous shaking. The mixture was then cooled rapidly to 20° and filtered on a large suction filter. The filtrate was concentrated at low temperature, the thick sirup being poured into two tared 6-liter flasks. One-fourth of its weight of dry sodium acetate and four times its weight of acetic anhydride were added to the sirup and the mixture was slowly heated on the steam-bath with vigorous shaking. As soon as the reaction started and the mixture boiled, it was quickly cooled in ice water to prevent foaming. When the reaction had quieted down the solution was boiled for five minutes and the contents of each flask was poured with constant stirring into about 8 liters of water. At first a dark, sticky reaction product formed which was separated by decantation and allowed to solidify under fresh water. A purer product gradually separated from the decanted solution on standing for a few days. The crude octa-acetate was recrystallized first from 50% alcohol and then from absolute methyl alcohol (with the aid of decolorizing carbon) until a pure product was obtained.

α -chloro-hepta-acetyl gentiobiose proceeds at least in two definite steps. Preliminary experiments showed that α -octa-acetylgentiobiose and β -penta-acetylglucose seem to follow the same procedure in this reaction. Schlubach [*Ber.*, 59, 840 (1926)] and Brigl and Keppler [*Ber.*, 59, 1588 (1926)] have already prepared β -chloro-acetyl glucose and similar β derivatives by other methods.

⁶ Hudson and Johnson, *THIS JOURNAL*, 39, 1274 (1917).

⁷ Haworth and Wylam, *J. Chem. Soc.*, 123, 3122 (1923).

α -Fluoro-hepta-acetylgentiobiose was prepared from **β -octa-acetylgentiobiose** in the manner previously described.⁸ It is important to finish the distillation as quickly as possible (in twenty minutes instead of half an hour). The sirup was crystallized by stirring with some methyl alcohol, the yield of impure crystals being 7 g. from 15 g. of **β -octa-acetate**. It was recrystallized several times by dissolving in boiling methyl alcohol with addition of decolorizing carbon, filtering through hardened paper with the aid of a hot-water funnel and allowing the filtrate to cool gradually. The pure product crystallizes in small needles and is stable, colorless and tasteless. It is fairly soluble in benzene, slightly soluble in petroleum ether, water and cold methyl alcohol; m. p. 168–169° (Helferich, Bäuerlein and Wiegand, 162–163°).⁹ The determination of the specific rotation in chloroform gave the following result.

Rotation. Third recrystallization. Subs., 0.6358: $\alpha = +4.325^\circ$; $[\alpha]_D^{20} = +42.48^\circ$. Fourth recrystallization. Subs., 0.6015: $\alpha = +4.142^\circ$; $[\alpha]_D^{20} = +42.99^\circ$. Fifth recrystallization. Subs., 0.6303: $\alpha = +4.384^\circ$; $[\alpha]_D^{20} = +43.43^\circ$. Sixth recrystallization. Subs., 0.6251: $\alpha = +4.384^\circ$; $[\alpha]_D^{20} = +43.79^\circ$. Seventh recrystallization. Subs., 0.6142: $\alpha = +4.280^\circ$; $[\alpha]_D^{20} = +43.51^\circ$.

Therefore, $+43.80^\circ$ is taken as the specific rotation of the pure substance, since another preparation gave as the final rotation $+43.85^\circ$.

Anal. Subs., 0.2091: CO_2 , 0.3738; H_2O , 0.1017. Subs., 0.5168: CaF_2 , 0.0299. Subs., 0.5000: 100.00 cc. of 0.25 *N* H_2SO_4 , 312.10 cc. of 0.1 *N* NaOH . Subs., 0.0516, 0.0866: C_6H_6 , 100 g., Δf , 0.028°, 0.040°. Calcd. for $\text{C}_{26}\text{H}_{36}\text{O}_{17}\text{F}$: C, 48.88; H, 5.53; F, 2.97; 62.67 cc. of 0.1 *N* NaOH for $\text{AcOH} + \text{F}$; mol. wt., 638. Found: C, 48.76; H, 5.44; F, 2.81; 62.10 cc. of 0.1 *N* NaOH ; mol. wt., 554, 651.

α -Chloro-hepta-acetylgentiobiose.—Many experiments were made before suitable conditions were found to obtain this derivative. The use of zinc chloride in the reaction is especially essential. Besides the two reactions mentioned in the introduction, another reaction is noticeable in which probably a dichloro compound is formed. This dichloro compound is not easily separated from the monochloro compound, the best means found being recrystallization from methyl alcohol. In order to prevent its formation as far as possible, it is necessary to follow exactly the description of the preparation as to time and temperature.

A tube 25 cm. long and 5 cm. in diameter was closed at one end and sealed at the other end to a tube 1 cm. in diameter and 7 cm. long. This tube was used as a container for saturating with hydrochloric acid a suspension of 10 g. of dry **β -octa-acetylgentiobiose** in a solution of 3 g. of zinc chloride in 100 cc. of pure acetic anhydride. The hydrochloric acid was washed by passage through sulfuric acid and then through acetic anhydride, after which it was passed through a glass spiral tube provided with a bulb pocket at the lower end for condensing acetic anhydride vapor (by cooling the spiral in an ice-and-salt mixture). A slow stream of hydrogen chloride thus prepared was passed through the described solution of gentiobiose octa-acetate, the container being cooled in ice and salt. Saturation was completed in about three hours. The tube was sealed and kept for twenty-two hours at 3 to 5°. It was opened after cooling in ice and salt. The solution, after being concentrated by means of a current of dry air under a bell jar for one hour, was poured into a separatory funnel containing ice water, crushed ice and chloroform and was shaken out 4 times with water. The chloroform solution was dried with calcium chloride and concentrated at low temperature to a sirup which crystallized readily when stirred with ether. The crystals were separated on a suction filter. Recrystallization was first performed by adding ether to a concentrated

⁸ Brauns, *THIS JOURNAL*, 45, 834 (1923).

⁹ Ref. 2 a, p. 36.

chloroform solution. Repeated recrystallizations did not remove all impurities, as the chlorine content was always found to be too high. Good results were obtained by making a concentrated solution in hot methyl alcohol, adding some decolorizing carbon, filtering through hardened paper with the aid of a hot-water funnel and cooling the solution in ice and afterwards in ice and salt.

The crystals were separated on a suction filter and dried in a vacuum desiccator; *m. p.* 148°. The determination of the specific rotation in chloroform gave the following results.

Rotation. First recrystallization. Subs., 0.4434: $\alpha = +5.684^\circ$; $[\alpha]_D^{20} +80.04^\circ$. Second recrystallization. Subs., 0.4642: $\alpha = +5.961^\circ$; $[\alpha]_D^{20} +80.18^\circ$. Third recrystallization. Subs., 0.6431: $\alpha = +8.276^\circ$; $[\alpha]_D^{20} +80.36^\circ$. Fourth recrystallization. Subs., 0.6476: $\alpha = +8.370^\circ$; $[\alpha]_D^{20} +80.70^\circ$. Fifth recrystallization. Subs., 0.6289: $\alpha = +8.117^\circ$; $[\alpha]_D^{20} +80.59^\circ$. Sixth recrystallization. Subs., 0.6491: $\alpha = +8.370^\circ$; $[\alpha]_D^{20} +80.51^\circ$; 0.6185: $\alpha = +7.978^\circ$; $[\alpha]_D^{20} +80.54^\circ$; 0.6495: $\alpha = +8.373^\circ$; $[\alpha]_D^{20} +80.50^\circ$.

The average of the last crystallization, $+80.52^\circ$, is taken as the specific rotation of the pure substance. The pure solution crystallizes in needles and is tasteless, colorless and stable. It is readily soluble in ordinary solvents except water, petroleum ether and ether.

Anal. Subs., 0.2377: CO_2 , 0.4172; H_2O , 0.1134. Subs., 0.2477, 0.2501: AgCl , 0.0535, 0.0523. Subs., 0.5000: 310.53 cc. of 0.1 *N* NaOH ; 249.25 cc. 0.1 *N* H_2SO_4 . Subs., 1.3392, 2.5513: C_6H_6 , 100 g., Δf , 0.114°, 0.202°. Calcd. for $\text{C}_{28}\text{H}_{48}\text{O}_{17}\text{Cl}$: C, 47.65; H, 5.39; Cl, 5.41; 61.10 cc. of 0.1 *N* NaOH ; mol. wt., 655. Found: C, 47.50; H, 5.33; Cl, 5.34; 5.17; 61.28 cc. of 0.1 *N* NaOH ; mol. wt., 588, 631.

α -Bromo-hepta-acetylgentiobiose.—Thirty grams of octa-acetylgentiobiose was dissolved in 300 cc. of purified chloroform and cooled to about 0° in an ice-and-salt mixture, 75 cc. of a saturated solution of hydrogen bromide in acetic acid (also cooled to 0°) being added. The mixture was kept in a stoppered Erlenmeyer flask in ice water for one and one-half hours, then was poured into a separatory funnel containing ice water and cracked ice and shaken out 4 times with ice water. The chloroform extract was dried with calcium chloride, filtered and evaporated to a sirup at low temperature. Dry ether was added and by evaporating and stirring, the sirup was brought to crystallization. The crystals were filtered by suction and recrystallized by dissolving in a small amount of purified chloroform and gradually adding ether to the filtered solution. The first separation contained most of the impurities. The recrystallization was repeated until a constant rotation was obtained; *m. p.* 144°. The solutions for the rotations were prepared with purified chloroform.

Rotation. First recrystallization. Subs., 0.6049: $\alpha = +9.770^\circ$; $[\alpha]_D^{20} +100.85^\circ$. Second recrystallization. Subs., 0.6061: $\alpha = +9.808^\circ$; $[\alpha]_D^{20} +101.04^\circ$. Third recrystallization. Subs., 0.6113: $\alpha = +9.895^\circ$; $[\alpha]_D^{20} +101.06^\circ$; 0.6343: $\alpha = +10.269^\circ$; $[\alpha]_D^{20} +101.08^\circ$. Fourth recrystallization. Subs., 0.6301: $\alpha = +10.206^\circ$; $[\alpha]_D^{20} +101.14^\circ$; 0.6383: $\alpha = +10.328^\circ$; $[\alpha]_D^{20} +101.03^\circ$.

Therefore, $+101.08^\circ$ is taken as the specific rotation of the pure substance. It is not stable but can be kept in a desiccator over sodium hydroxide in an ice box. It crystallizes in colorless needles and is tasteless. It is soluble in ordinary solvents except water, petroleum ether and ether. Zemplén,¹⁰ who first described crystalline bromo-hepta-acetylgentiobiose, found *m. p.* 132–133.5° and $[\alpha]_D^{19} +111.8^\circ$. Probably Zemplén's preparation contained some dibromo derivative, as is also indicated by the bromine determination (found 12.06% Br).

¹⁰ Zemplén, *Ber.*, 57, 702 (1924).

Anal. Subs., 0.2757: CO_2 , 0.4530; H_2O , 0.1207. Subs., 0.3146, 0.3126: AgBr , 0.0864, 0.0859. Subs., 0.5000: 306.44 cc. of 0.1 *N* NaOH ; 249.25 cc. of 0.1 *N* H_2SO_4 . Subs., 1.0431, 1.7316: C_6H_6 , 100 g., Δ_f , 0.082°, 0.135°. Calcd. for $\text{C}_{28}\text{H}_{40}\text{O}_{17}\text{Br}$: C, 44.62; H, 5.05; Br, 11.43; 57.20 cc. of 0.1 *N* NaOH ; mol. wt., 699. Found: C, 44.81; H, 4.90; Br, 11.68, 11.69; 57.19 cc. of 0.1 *N* NaOH ; mol. wt., 636, 641.

α -Iodo-hepta-acetylgentiobiose.—Five grams of gentiobiose octa-acetate was dissolved in 10 cc. of methylene chloride in a Pyrex test-tube and a minute amount of zinc iodide was added. The solution was cooled in an ice-and-salt bath. Hydriodic acid (which was first passed through asbestos mixed with red phosphorus, then through a calcium chloride tower, then through a phosphorus pentoxide tube and finally through a spiral tube cooled in ice and salt) was passed in a slow stream through the gentiobiose octa-acetate solution for ten to fifteen minutes. The solution was poured into a dish and evaporated with a dry current of air under a bell jar. The residue was stirred with petroleum ether, the solution was poured off and this process repeated until crystallization started. The crystals were mixed with dry ether, filtered by suction and washed with small amounts of ether. Recrystallization was produced by dissolving in a small amount of purified chloroform and gradually adding ether. The first separation contains most of the colored impurities. The recrystallization was repeated until a constant rotating substance was obtained.

The pure compound decomposes at 134° forming a dark brown liquid. The determination of the specific rotation in chloroform gave the following results.

Rotation. First recrystallization. Subs., 0.4524: $\alpha = +9.080^\circ$; $[\alpha]_D^{20} +125.32^\circ$. Second recrystallization. Subs., 0.5555: $\alpha = +11.212^\circ$; $[\alpha]_D^{20} +126.02^\circ$. Third recrystallization. Subs., 0.5270: $\alpha = +10.640^\circ$; $[\alpha]_D^{20} +126.06^\circ$.

Therefore, +126.10° is taken as the specific rotation of the pure substance. The pure compound crystallizes in long needles and is tasteless and colorless. It is not stable but can be kept in a pure condition for many months in a desiccator over sodium hydroxide in an ice box. It is readily soluble in the ordinary solvents except water, petroleum ether and ether.

Anal. Subs., 0.2477: CO_2 , 0.3788; H_2O , 0.1092. Subs., 0.2157: AgI , 0.0688. Calcd. for $\text{C}_{28}\text{H}_{40}\text{H}_{17}\text{I}$: C, 41.82; H, 4.73; I, 17.02. Found: 41.71; H, 4.94; I, 17.24.

α - and β -Chloro-hepta-acetylgentiobiose.—Two grams of β -octa-acetylgentiobiose was dissolved in 20 cc. of acetic anhydride and saturated in an ice-and-salt bath with hydrochloric acid in the manner described for the preparation of the α -chloro derivative, except that no zinc chloride was added. The tube was sealed and kept for three hours at 15°; then it was cooled in an ice-and-salt bath and opened, the solution being poured into an evaporating dish and evaporated for half an hour with a current of dry air. The remaining solution was diluted with purified chloroform and poured into a separatory funnel containing ice water and cracked ice. The chloroform solution was quickly shaken out 3 times with ice water, dried with calcium chloride and evaporated with a rapid dry current of air to a sirup which was stirred with ether and soon solidified to a crystalline mass which was then thinned with ether, the crystals were filtered on a suction filter and dried in a vacuum desiccator. The determination of the specific rotation of 0.4651 g. of substance in purified chloroform gave the results shown in Table III. The tabulation shows a change from a negative to a positive rotation. A Carius determination gave the following result. Subs., 0.2458: AgCl , 0.0597; calcd. for a monochloro-derivative, $\text{C}_{28}\text{H}_{40}\text{O}_{17}\text{Cl}$, 5.42% Cl. Found: 6.0% Cl. A small amount of dichloro-derivative is therefore present in the reaction product. Calculated according to Hudson's method [Hudson, THIS JOURNAL, 46, 462, 476, 2600 (1924)] taking the specific rotation of α -chloro-hepta-acetylgentiobiose (mol. wt. 655, $[\alpha]_D = +80.5$) and Hudson's coefficient $B_{\text{gentiobiose}} = +15,900$ as a basis, the specific rotation of

TABLE III
 SPECIFIC ROTATION

Time after solution	α	$[\alpha]_D^{20}$
10 min.	-0.520	- 7.0°
30 min.	-0.450	- 6.0
1 hr.	-0.398	- 5.3
2 hr.	-0.312	- 4.2
5 hr.	-0.03	- 0.5
45 hr.	+1.473	+19.8

β -chloro-hepta-acetylgentiobiose should be $(B_{\text{gentiobiose}} - A_1)/655 = 15,900 - [(80.5(655) - 15,900)]/655 = -32$, from which it is concluded that at least three-fourths of the reaction product is β -chloro-hepta-acetylgentiobiose. This indicates that the β -chloro derivative is formed first and is then converted into the α -chloro derivative. A preliminary experiment was made for the purpose of converting the impure β -chloro-hepta-acetylgentiobiose with silver carbonate and methyl alcohol into the α -methyl derivative. A colorless sirup which could not be brought to crystallization was obtained.

α - and β -Iodo-hepta-acetylgentiobiose.—Eight grams of β -gentiobiose octa-acetate was dissolved in 16 cc. of methylene chloride and the solution was saturated in an ice-and-salt bath with hydriodic acid in the manner described for the preparation of the α -iodo derivative, no zinc chloride being added. The light brown solution was quickly evaporated in a current of dry air. On stirring with petroleum ether the residue solidified to a mass of needles which was dissolved in a small quantity of purified chloroform. Ether was added until crystallization started. The crystals which separated were washed with ether on a suction filter. They were sticky and contained iodine. Probably the recrystallization had partly converted the α - into the β -iodo derivative. The determination of the specific rotation of 0.1674 g. of substance in purified chloroform gave the following result.

Time after solution	α	$[\alpha]_D^{20}$
6 min.	-0.381	-14.2°
10 min.	-0.268	-10.3
20 min.	-0.208	- 7.7
30 min.	-0.173	- 6.5
1 hr.	-0.035	- 1.3
24 hr.	+2.045	+76.3
48 hr.	+2.530	+94.4
72 hr.	+2.634	+98.3

After twenty-four hours the solution gradually turned brown. Calculated according to Hudson's method, taking the specific rotation of α -iodo-hepta-acetylgentiobiose (mol. wt. 746, $[\alpha]_D = +126.1$) and Hudson's coefficient $B_{\text{gentiobiose}} = +15,900$ as a basis, the specific rotation of β -iodo-hepta-acetylgentiobiose should be $(B_{\text{gentiobiose}} - A_1)/746 = (15,900 - [(126.1)(746) - 15,900])/746 = -83$, from which it is concluded that at least 67% of the reaction product is β -iodo-hepta-acetylgentiobiose. This supports the conclusion reached in the case of the chloro derivative that in this reaction the β halogen derivative is formed first and is subsequently converted into the α -halogen derivative.

Summary

The α -fluoro-, chloro-, bromo- and iodo-hepta-acetyl derivatives of gentiobiose have been prepared and described. A comparison of the

specific rotational values of these halogen derivatives shows that these straight chain biose derivatives behave the same as the branched chain biose derivatives investigated in the previous article, as agreement with the regular relationship observed for the corresponding derivatives of the monose sugars is obtained only by excluding the values for the fluoro derivatives.

Besides the pure α -halogen derivatives of gentiobiose, impure β -chloro and iodo compounds were obtained.

The Walden inversion from β -octa-acetylgentiobiose to α -chloro- and iodo-hepta-acetyl gentiobiose by the action of hydrochloric and hydriodic acids proceeds at least in *two* definite steps, β -chloro- or iodo-hepta-acetyl-gentiobiose being intermediately formed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF SASKATCHEWAN]

ACYL *ISO*-UREAS

BY S. BASTERFIELD AND MYRON S. WHELEN

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The chemistry of methyl- and ethyl-*iso*-ureas (oxygen ethers of urea) and their acyl derivatives has been studied mainly by Stieglitz and his collaborators,^{1,2,3} and by Wheeler and Johnson.⁴

More recently E. A. Werner⁵ has made important contributions to this field of study.

In an investigation of the pharmacological properties of acyl *iso*-ureas, it was observed by one of us⁶ that carbethoxy-ethyl-*iso*-urea was mildly depressing to the central nervous system and caused a large and rapid fall of body temperature. Later it was shown that dicarbethoxy-ethyl-*iso*-urea possessed similar properties but in greater degree⁷ while carbo-*n*-butoxy-ethyl-*iso*-urea had only slight physiological action.⁸

In view of these results, the preparation of a greater variety of acyl *iso*-ureas was undertaken. Since only methyl- and ethyl-*iso*-ureas and their derivatives have been prepared up to the present, a study of the possibility of obtaining propyl-, butyl-, phenyl-, benzyl- and phenylethyl-*iso*-ureas was commenced, preliminary results of which are reported in this

¹ Dains, *THIS JOURNAL*, **21**, 136 (1899).

² Bruce, *ibid.*, **26**, 419 (1904).

³ McKee, *Am. Chem. J.*, **26**, 209 (1901).

⁴ Wheeler and Johnson, *ibid.*, **24**, 189 (1900).

⁵ Werner, *J. Chem. Soc.*, **105**, 923 (1914); "The Chemistry of Urea," Longmans, London and New York, 1923.

⁶ Basterfield, *J. Pharmacol.*, **20**, 451 (1923).

⁷ Basterfield and Paynter, *THIS JOURNAL*, **48**, 2176 (1926).

⁸ Basterfield, Woods and Wright, *ibid.*, **48**, 2371 (1926).

paper. A considerable number of new acyl derivatives of methyl- and ethyl-*iso*-ureas are also described.

The *iso*-urea hydrochlorides were prepared by the method of Stieglitz and Bruce² which consists in the addition of anhydrous alcohols to cyanamide in the presence of dry hydrogen chloride. The acyl derivatives were obtained by treating the *iso*-urea hydrochlorides in ether suspension with the required amount of acyl halide, the whole being shaken with concentrated aqueous potassium or sodium hydroxide. Details of purification are given in the experimental part of the paper.

The addition of *n*-propyl and *n*-butyl alcohols to cyanamide was found to take place much less readily than that of methyl and ethyl alcohols. The hydrochlorides of *n*-propyl and *n*-butyl-*iso*-ureas were obtained but could not be satisfactorily purified. A fairly pure sample of *n*-propyl-*iso*-urea was obtained as an oil and acyl derivatives of both *iso*-ureas were prepared in pure condition. Work on benzyl- and phenylethyl-*iso*-ureas is in progress.

Experimental Part

I. Derivatives of Methyl-*iso*-urea

Data on yields, melting points and analyses are given in Table I.

Phenylacetylmethyl-*iso*-urea, $C_6H_5CH_2CONHC(OCH_3)NH$.—This was obtained as an oil which was decomposed somewhat by distillation under reduced pressure. The oil was dissolved in anhydrous ether and the solution treated with dry hydrogen chloride. The precipitated hydrochloride was analyzed for chlorine by titration with a standard solution of silver nitrate.

Chloro-acetylmethyl-*iso*-urea, $CH_2ClCONHC(OCH_3)NH$.—This was obtained as an oil which was converted into the hydrochloride and analyzed for displaceable chlorine. The salt was purified by recrystallization from ethyl alcohol.

Carbo-*n*-propoxymethyl-*iso*-urea, $C_3H_7OCONHC(OCH_3)NH$.—This compound, prepared from methyl-*iso*-urea and *n*-propyl chlorocarbonate, was obtained as an oil which rapidly solidified in a desiccator. It was recrystallized from ligroin.

An attempt to prepare the hydrochloride yielded only *n*-propyl-allophanic ester; m. p. 167°. The salt is evidently unstable and loses methyl chloride even at room temperature. The allophanic ester was further identified by analysis.

Anal. Calcd. for $C_5H_{10}N_2O_3$: N, 19.17. Found: 19.02.

Carbo-*n*-butoxymethyl-*iso*-urea, $C_4H_9OCONHC(OCH_3)NH$.

Carbo-*iso*-amoxymethyl-*iso*-urea, $C_6H_{11}OCONHC(OCH_3)NH$.—This was obtained

TABLE I
DERIVATIVES OF METHYL-*iso*-UREA

Derivative	Formula	Yield, %	M. p., °C.	Analyses, %	
				Calcd.	Found
Phenylacetyl	$C_{10}H_{12}N_2O_3$	85	207 (dec.) ^a	Cl 15.51 ^a	15.61 15.62
Chloro-acetyl	$C_4H_7N_2O_3Cl$	Poor	183 ^a	Cl 18.95 ^a	18.80 18.70
Carbo- <i>n</i> -propoxy	$C_6H_{12}N_2O_3$..	36–37	N 17.50	17.52 17.56
Carbo- <i>n</i> -butoxy	$C_7H_{14}N_2O_3$	67	32	N 16.09	16.06 15.96
Carbo- <i>iso</i> -amoxy	$C_8H_{16}N_2O_3$	94	93	N 14.88	14.71

^a M. p. of hydrochloride and percentages of displaceable chlorine.

as an oil which did not solidify readily. It was taken up in ligroin and cooled in a freezing mixture. Crystals were obtained in small quantity. Treatment with dry hydrogen chloride in ether gave *iso*-amyl allophanic ester, m. p. 162°.

TABLE II
DERIVATIVES OF ETHYL-*iso*-UREA

Derivative	Formula	Yield, %	M. p., °C.	Analyses, %		
				Calcd.	Found	
Phenylacetyl	C ₁₁ H ₁₄ N ₂ O ₂	90	(b. p. 160, 20 mm.)	N 13.59	13.68	13.78
<i>p</i> -Nitrobenzoyl	C ₁₀ H ₁₁ N ₃ O ₄	90	125	N 17.73	17.76	17.60
α -Bromopropionyl	C ₆ H ₁₁ N ₃ O ₂ Br	100	141	N 12.58	12.76	12.68
Chloro-acetyl	C ₆ H ₉ N ₂ O ₂ Cl	V. poor ^a	140 ^a	N 14.04 ^a	13.94	
				Cl 17.76 ^a	17.85	17.90
Carbo- <i>n</i> -propoxy	C ₇ H ₁₄ N ₂ O ₃	-100 ^b	...	N 16.09	16.17	16.12
Carbo- <i>iso</i> -amoxy	C ₉ H ₁₈ N ₂ O ₃	-100 ^b	-10	N 13.86	13.96	13.94
Benzenesulfonyl	C ₉ H ₁₂ N ₂ O ₃ S	92	{ 86	N 12.28	12.24	12.20
			{ 101	N 12.28	12.28	

^a Yield and m. p. of and percentages of N and Cl for hydrochloride.

^b Almost quantitative yield.

II. Derivatives of Ethyl-*iso*-urea.

See Table II for further data on these derivatives.

Phenylacetylethyl-*iso*-urea, C₆H₅CH₂CONHC(OC₂H₅)NH.—This compound was an oil which was purified by distillation under reduced pressure.

***p*-Nitrobenzoylethyl-*iso*-urea**, NO₂C₆H₄CONHC(OC₂H₅)NH.—Slightly yellow crystals from ether.

α -Bromopropionylethyl-*iso*-urea, CH₃CHBrCONHC(OC₂H₅)NH.—This was obtained as an oil which was decomposed by distillation under reduced pressure. After standing for several months, the oil had deposited a quantity of white crystals. The solid was insoluble in ether but was soluble in warm alcohol. It was at first thought that the substance might be 2-ethoxy-4-methylhydantoin but analysis showed the required nitrogen content for α -bromopropionylethyl-*iso*-urea. The insolubility in ether, however, suggests that the solid is a polymer, the original oil being the unpolymerized compound.

Chloro-acetylethyl-*iso*-urea, CH₂ClCONHC(OC₂H₅)NH.—The base, a viscid oil, was converted into the hydrochloride.

Carbo-*n*-propoxy-ethyl-*iso*-urea, C₃H₇OCONHC(OC₂H₅)NH.—The clear oil first obtained solidified in a freezing mixture. Analysis showed it to be quite pure.

Carbo-*iso*-amoxy-ethyl-*iso*-urea, C₆H₁₁OCONHC(OC₂H₅)NH.—The oil first obtained was found to be quite pure.

Benzenesulfonylethyl-*iso*-urea, C₆H₅SO₂NHC(OC₂H₅)NH.—This compound was obtained as a solid, crystallizing from alcohol in large, rhombic prisms. The first sample melted at 86°. After standing for a few weeks the crystals were yellowish and moist. The substance was recrystallized, m. p. 76°. In the course of a few days the melting point had risen to 101°. Repeated recrystallizations gave fractions with different melting points, the highest being 110°. All fractions melted at 101° after standing for a few days. The material melting at 101° had exactly the same nitrogen content as the original substance. The phenomenon is probably due to di- or polymorphism.

III. *n*-Propyl-*iso*-urea, NH₂C(OC₃H₇)NH

Five g. of cyanamide was dissolved in 250 cc. of *n*-propyl alcohol and the calculated amount of dry hydrogen chloride passed into the solution cooled in ice. After standing

for three days, the liquid gave no reaction for cyanamide. The alcohol was removed by distillation under reduced pressure. A viscous, semi-solid mass was left which became almost completely solid after prolonged standing in a vacuum desiccator. Recrystallization from alcohol even at low temperatures was unsuccessful. Concentrated alcoholic solutions poured into ether or ligroin at -20° gave only semi-solid products. The nearly solid mass obtained after long standing in a desiccator was very hygroscopic and became sirupy in a few minutes after exposure to the air.

From a sample of this impure hydrochloride, the free base was liberated by treatment with a large excess of powdered potassium hydroxide in ether suspension. The ether solution on evaporation yielded a slightly yellow oil of very obnoxious and penetrating odor. It was dried in a vacuum and analyzed without further purification.

Anal. Calcd. for $C_6H_{10}N_2O$: N, 27.27. Found: 27.27, 27.40.

Benzoyl-*n*-propyl-*iso*-urea, $C_6H_5CONHC(OC_3H_7)NH$.—The impure propyl-*iso*-urea hydrochloride from 5 g. of cyanamide was converted into the benzoyl derivative by the usual method. The product was an oil which was appreciably contaminated with propyl alcohol. It was taken up in ether and treated with dry hydrogen chloride. The precipitated hydrochloride was recrystallized from alcohol. It melted at 97° with evolution of *n*-propyl chloride. The yield was good but a portion was accidentally lost and the exact yield was not determined.

Anal. Calcd. for $C_{11}H_{14}N_2O_2 \cdot HCl$: Cl, 14.73. Found: 14.92, 14.85.

IV. *n*-Butyl-*iso*-urea Hydrochloride, $NH_2C(OC_4H_9)NH \cdot HCl$

When hydrogen chloride was passed into a butyl alcohol solution of cyanamide (5 g. in 250 cc.) a fine, white, crystalline precipitate was rapidly formed. This was found to be the dihydrochloride of cyanamide, the latter acting in the di-imide form as a diacid base. To minimize the separation of this compound, 200–300 cc. more alcohol was used and an excess of hydrogen chloride carefully avoided. The reaction mixture stood for a month before the reaction for cyanamide had disappeared. The liquid had meanwhile assumed a reddish-brown color. When the alcohol had been removed by distillation in a vacuum, a red, semi-solid mass was obtained. Attempts to purify this were fruitless, but the presence of *n*-butyl-*iso*-urea was proved by the preparation from the impure product of the *p*-nitrobenzoyl derivative.

***p*-Nitrobenzoyl-*n*-butyl-*iso*-urea**, $NO_2C_6H_4CONHC(OC_4H_9)NH$.—The impure butyl-*iso*-urea hydrochloride was suspended in ether and treated with the required quantity of *p*-nitrobenzoyl chloride in the presence of aqueous potassium hydroxide. The ether phase yielded on evaporation a pale yellow solid. Recrystallized from ether it melted at 118° .

Anal. Calcd. for $C_{12}H_{16}N_2O_4$: N, 15.84. Found: 15.76, 15.80.

Summary

1. A number of new acyl derivatives of methyl- and ethyl-*iso*-ureas have been prepared.

2. The addition of *n*-propyl and *n*-butyl alcohols to cyanamide has been studied and the impure hydrochlorides of *n*-propyl and *n*-butyl-*iso*-ureas have been obtained. *n*-Propyl-*iso*-urea has been obtained as an oil sufficiently pure for analysis, and its benzoyl derivative prepared and analyzed as the hydrochloride. *n*-Butyl-*iso*-urea has been characterized by the preparation and analysis of its *p*-nitrobenzoyl derivative.

SASKATOON, SASKATCHEWAN, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

AN APPARATUS FOR DETERMINING BOTH THE QUANTITY OF GAS EVOLVED AND THE AMOUNT OF REAGENT CONSUMED IN REACTIONS WITH METHYL MAGNESIUM IODIDE

BY E. P. KOHLER, J. F. STONE, JR., AND R. C. FUSON

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Methyl magnesium iodide has long been used as a valuable and, in most cases, a reliable reagent for ascertaining the number of active hydrogen atoms in an organic compound.¹ This is accomplished by measuring the methane evolved when a known weight of substance reacts with excess of the reagent in an apparatus devised by Zerewitinoff² which admirably serves this purpose.

A number of Grignard reactions—notably those involving oxidation and reduction—are accompanied by evolution of gas which is not due to the presence of active hydrogen. In order to follow the course of these reactions it is necessary to know the quantity of reagent consumed as well as the amount of gas evolved. The apparatus herein described was designed for the study of such reactions. Once at hand it has been employed for getting information on the structure of a great variety of organic compounds, and has proved so useful that it seemed advisable to make it available to others with similar problems.

The Apparatus³

The apparatus is shown in Fig. 1. *A* is a 500cc. cylindrical reservoir used for storing the solution of the reagent. It is attached to the apparatus by a ground-glass joint and contains a glass tube *a* which connects it to the buret *B* through the by-pass in the special stopcock *C*. At the top the reservoir is connected by a glass tube *b* to the stopcock *c*. Stopcocks *c* and *d* are 120° three-way stopcocks whose use will be described below, *B* is a 10cc. buret graduated in twentieths of a cc. *D* is a 5cc. buret graduated in tenths of a cc. The special stopcock *C*⁴ carries, in addition to the by-pass, an ordinary three-way stopcock arrangement for con-

¹ Houben, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, 1924, second edition, Vol. 4, p. 732.

² Zerewitinoff, *Ber.*, 40, 2026 (1907).

³ An apparatus essentially like this was first designed by J. F. Stone, Jr., for the investigation of nitro compounds. After several years' experience it was redesigned and simplified by R. C. Fuson. The quantitative results published herewith were obtained with the new apparatus.

⁴ Instead of this special stopcock the original apparatus had a rubber stopper with four holes through which passed inlet and outlet tubes, and the ends of the two burets. In that form the apparatus can be constructed from materials generally available. It gives satisfactory results with substances that react rapidly but when long heating is necessary the rubber stopper consumes reagent and evolves gas.

necting *B* and *D* in turn with the reaction chamber *E*. The reaction chamber consists of a 40cc. flat-bottomed flask attached by a ground-

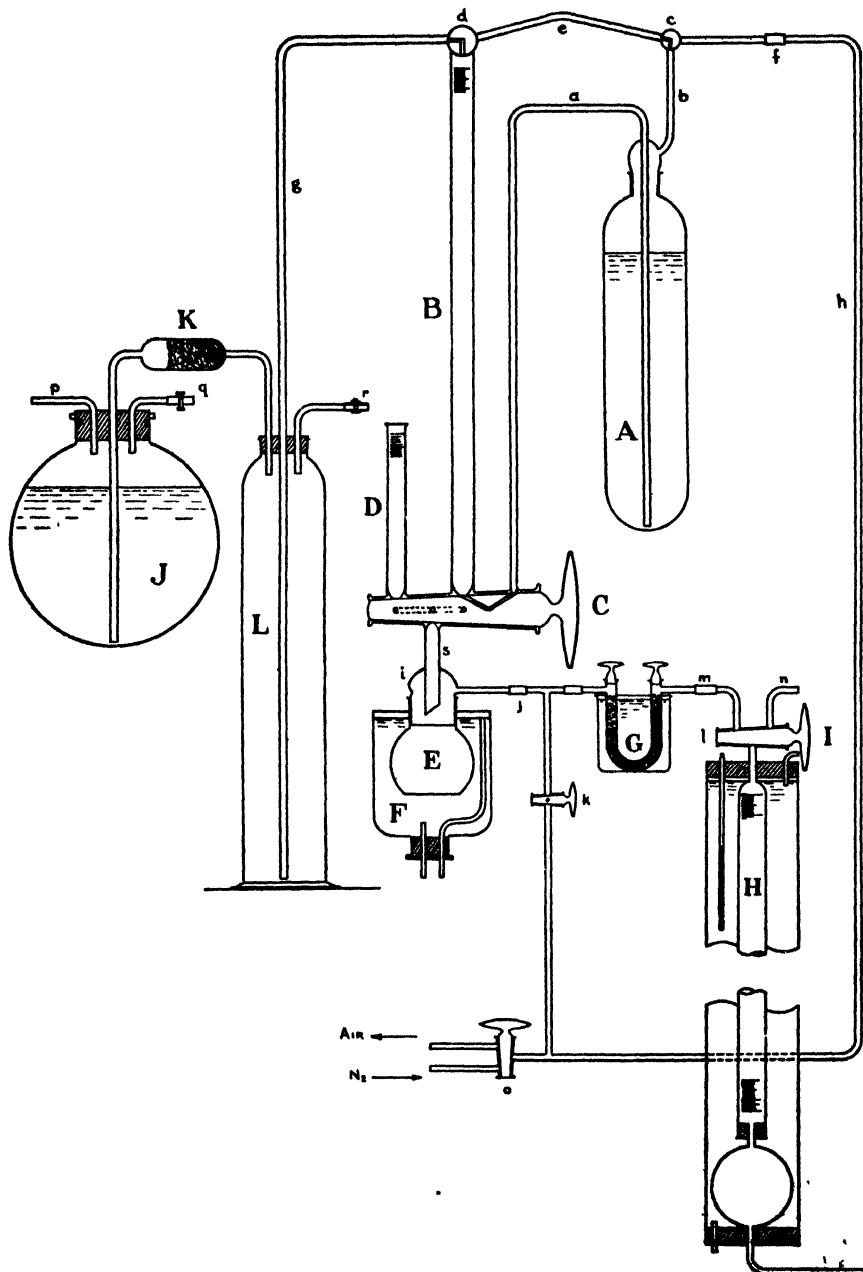


Fig. 1.

glass joint to the shoulder *i*. In the present work four such flasks were made, each being ground to fit *i*; this was done to allow for breakage and to avoid delays due to cleaning. *E* is immersed in a bath *F* which serves as a temperature regulator. From the shoulder *i* a tube for gas leads to a U-tube *G* packed with glass beads and phosphorus pentoxide. In order that its temperature may not undergo any sudden change, *G* is kept in a beaker of water at room temperature. The U-tube is connected to a gas buret *H*. This buret is an ordinary 50cc. gas buret graduated in tenths of a cc. and equipped with a special capillary stopcock *I* which serves not only to connect the buret in turn with the capillary arms *m* and *n* but has in addition a special vent *l* which serves to connect *m* with the air. The buret is filled with mercury and has at its base a 20cc. overflow bulb which is connected with a leveling bulb. It is enclosed in a Victor Meyer jacket filled with water and carrying a thermometer. The tube *g* serves ordinarily to connect to the air through *d* but during the process of filling it is attached to the system *J-K-L* which will be described later. *A*, *B*, *C*, *D* and *E* are made of Pyrex glass.

The Preparation of the Reagent

The Grignard reagent used is a solution of methyl magnesium iodide in *iso*-amyl ether containing approximately 0.8 mole of active reagent per liter. In preparing it pure dry materials are used and the operations are carried out as far as possible in an atmosphere of pure dry nitrogen.⁵

The following procedure is used. One hundred g. of *iso*-amyl ether and 8 g. of magnesium are placed in a 500cc. round-bottom wetted-neck flask equipped with a stirrer, dropping funnel and a tube for introducing dry nitrogen. Forty g. of methyl iodide is dropped in during the course of an hour, the reaction flask being continually swept by a current of dry nitrogen and maintained at a temperature between 0 and 20°. The reagent is then diluted by the addition of 175 g. of *iso*-amyl ether. The flask is immersed in an oil-bath and heated for one and one-half hours at about 100°. After being allowed to stand overnight it is transferred to the apparatus.

Filling the Apparatus

For introducing the reagent solution into the reservoir *A* a special apparatus is attached to tube *g* as shown in Fig. 1. The flask *J* is the original vessel in which the

⁵ PURIFICATION OF THE NITROGEN.—Pure dry nitrogen was obtained by passing tank nitrogen successively through Fieser's solution, saturated lead acetate solution, concd. sulfuric acid and phosphorus pentoxide. The purification train consisted of the following ten parts connected in the order named: mercury trap (for pressure regulation), safety bottle, two wash bottles containing Fieser's solution,⁶ safety bottle, wash bottle containing lead acetate solution, safety bottle, two sulfuric acid drying towers, a Liebig duck partially filled with phosphorus pentoxide.

⁶ Fieser, THIS JOURNAL, 46, 2639 (1924).

reagent was made and is transferred to the position shown in Fig. 1 in such a way as to admit as little air as possible. *K* is a glass tube packed with glass wool for filtering the reagent. It leads into the settling tower *L* which carries the tube *g* leading to the apparatus.

Before *J* is placed in position the entire apparatus is cleaned, dried and filled with dry nitrogen. This is accomplished by washing successively with water, alcohol, ether and absolute ether. A rapid current of dry nitrogen is then passed through the apparatus for several hours. For this purpose *J* is replaced by an empty flask *J'* of the same size and stopcocks *c*, *d*, *C* and *o* are turned so that the nitrogen passes through the various parts of the apparatus in the following order: *J-K-L-g-B-a-A-b-h*. Stopcock *o* is turned so as to allow the nitrogen to escape into the air. In order to sweep the tube *e*, stopcocks *c* and *d* are turned so as to lead the gas directly from *g* to *h* through *e*. From time to time *o* is closed and *h* is opened so as to allow the gas to escape through the shoulder, the flask *E* being removed.

When the sweeping is complete *o*, *c*, *d* and *h* are closed and *J'* is replaced by *J* (containing the reagent). The reagent is then filtered through *K* into *L* by allowing nitrogen under suitable pressure to flow in at *p* and by opening *r* to the air. The reagent is allowed to settle in *L* and when clear or nearly so it is driven into the reservoir *A* by closing *r*, opening *o* to the air and turning *c* and *d* so that the solution flows from *g* into *B* and thence through the by-pass in *C* to the reservoir.

After the solution has been driven into *A*, stopcocks *c*, *d* and *C* are closed. *J*, *K* and *L* are then removed and *g* and *B* are cleaned by blowing successively dilute acid, water, alcohol and ether through the circuit *g-B-s* established by properly adjusting *d* and *C*. This circuit is then swept with dry nitrogen and the apparatus is ready for use.

Standardization of the Reagent Solution

Before the reagent solution can be used it must be standardized, that is, its strength in moles of active methyl magnesium iodide per liter must be determined. This is done in the following manner.

The reaction flask *E*, after being carefully cleaned, is heated in a free flame and allowed to cool in a vacuum desiccator. It is then placed in position, the ground-glass joint being lubricated with a small amount of good stopcock grease. If the grinding has been properly done, there will be little tendency for the flask to drop off and in case this seems likely the flask can be conveniently supported by a block placed in *F*. The bath *F* is now placed in the position shown in Fig. 1 such that *E* is almost entirely immersed. *C* is then turned so as to connect *D* and *s*, *h* is opened and nitrogen admitted at *o*. With *I* turned so as to connect *II* with *m*, the mercury level in *II* is raised until it stands a little above *I* in *m*. *I* is then closed. After the nitrogen has been passed through *D* and *E* for about twenty minutes *C* is turned so as to disconnect *s* and *D* and to connect *A* and *B* through the by-pass. *I* is now turned to connect *m* with the air through the vent *l*. The small amount of mercury in *m* is driven out and the circuit *G-m* is swept for a minute or two. *I* is then turned to connect *m* with *H* and *h* is closed after enough nitrogen has been allowed to flow into *H* to bring the mercury level down to the scale of the buret.

The Grignard reagent is now introduced. Stopcocks *o* and *c* are turned so as to admit nitrogen under pressure to *A*. *B* is then connected to *g* through *d*. The pressure of the nitrogen causes the solution to flow into *B*. When sufficient solution has been introduced into *B* the by-pass is closed by giving *C* an eighth of a turn in a clockwise direction; *c* and *d* are then closed. The level of the solution in *B* is now read as accurately as possible, by estimating to hundredths of a cc. With *d* still closed *C* is given a quarter turn in a clockwise direction. This brings the stopcock just beyond the posi-

tion for connecting *B* to *s* and must be done quickly. With *h* connected to *B* through *c*, *C* is turned back (in a counter-clockwise direction) far enough to allow the solution to run into *E*. In this way the desired volume of solution is introduced into *E*, and *C* is closed by a slight clockwise turn. It is well to keep the mercury level in *H* so adjusted that the pressure in *E* is always less than atmospheric. After a minute or two the level of the solution is read as before; the difference between this and the initial reading gives the volume of solution used. A measured volume of water is now introduced from *D* by turning *C* (clockwise direction) to connect *s* and *D*. To complete the reaction *F* is replaced by a beaker of water kept boiling by a small flame and the reaction flask is heated at 100° for at least five minutes. *F* is now replaced and brought to its initial temperature. After allowing at least fifteen minutes for the system to reach equilibrium the level in *H* is again read. The difference between this and the initial reading gives the total increase in volume of the system. To get the volume of gas produced by the reaction it is necessary to subtract from this the volume of reagent solution and of water introduced. We now have the total volume of gas obtained from a measured volume of Grignard reagent; from this the strength of the latter can be calculated. This may be conveniently expressed in terms of the amount of gas obtained per cc. of solution used. Thus a solution made up according to the directions given above will have a strength of about 16 cc. of gas per cc. of solution.

After a determination has been made *E* is removed and *D* is connected to *s*. Dilute acid, water, alcohol and ether are poured successively into *D* and allowed to run out through *s*. To clean the shoulder *i* it is sufficient to spray it with suitable solvents, usually alcohol followed by ether.

Use of the Apparatus

The apparatus is designed for the purpose of determining simultaneously two things—the amount of gas given off and the amount of Grignard reagent consumed by a given reaction. These ends are accomplished by the following procedure.

A weighed sample, usually about 0.2 g. of the compound to be studied, is placed in the reaction flask *E* which is then put in place and swept with nitrogen as described above. A measured volume of the Grignard reagent solution is now introduced, care being taken to use an amount in considerable excess of that required by theory. The reaction chamber is heated until the reaction ceases and the increase in volume is measured and the volume of evolved gas calculated in the manner previously described.

To find the amount of reagent consumed it is necessary only to determine the amount remaining unchanged at the end of the reaction and to subtract this from the total amount used. This is done by introducing a measured volume of water from *D* and determining the amount of Grignard reagent remaining by the procedure used in standardizing the solution. Thus in the case of acetanilide, for example, a sample weighing 0.2648 g. (0.00196 mole) was treated with 4.01 cc. of methyl magnesium iodide solution containing 0.7143 mole per liter or 0.00286 mole of Grignard reagent. The volume of evolved gas corrected to 0° and 760 mm. was 44.2 cc. or 0.00198 mole. By treating the excess Grignard reagent with

water 20.8 cc. or 0.00093 mole of gas was obtained. The amount of reagent consumed in the reaction is, therefore, $0.00286 - 0.00093 = 0.00193$ mole.

TABLE OF RESULTS
ALL QUANTITIES ARE EXPRESSED IN THOUSANDTHS OF A MOLE

Compound	Amt. of compd.	Amt. of reagent used	Gas from reaction	Gas from excess of reagent	Amt. of reagent consumed
Benzhydrol.....	0.99	1.80	1.01	0.82	0.98
Benzhydrol.....	1.00	1.80	1.03	.83	.97
Diphenylamine.....	0.98	2.25	1.05	1.26	.99
Benzophenone.....	1.77	2.90	0.03	1.16	1.74
Benzil.....	0.97	2.85	.09	0.90	1.95
Benzoin.....	1.08	2.82	1.10	.67	2.15
Dibenzoylmethane.....	0.50	1.80	0.53	.76	1.04*
Dibenzoylmethylmethane.....	.50	1.80	.08	.75	1.05*
Dibenzoylbromomethane.....	.50	1.80	.03	.78	1.02*
Acetanilide.....	1.96	2.86	1.98	.93	1.93
Benzyl benzamide.....	1.01	2.90	1.01	1.87	1.03
Acetophenone.....	2.28	2.90	0.33	0.63	2.27
Acetophenone.....	2.31	2.86	.36	.56	2.30
Desoxybenzoin.....	1.76	2.77	.10	.98	1.79
Triphenylethanone.....	1.15	2.79	.16	1.63	1.16
Acetomesitylene.....	0.95	1.35	.94	0.43	0.92*

The first two compounds contain only active hydrogen, the following two only carbonyl groups. The values obtained with these four substances indicate that under favorable conditions the apparatus makes it possible to determine both the gas evolved and the reagent consumed with an accuracy of about 3%. Benzoin and dibenzoylmethane, representing substances which contain both hydroxyl and carbonyl groups, give almost equally good results. In all these cases the reaction, including the escape of most of the gas from the solution, is rapid—most of the gas being collected within a few minutes.

The values obtained for the succeeding two compounds show that solutions of methyl- and bromodibenzoylmethane contain little if any enolic modification. Neither of these substances gives a copper compound when its ethereal solution is shaken with copper acetate, but the former is capable of forming a sodium compound while the latter apparently is not.⁷ The sodium compound of the methyl derivative may be formed as a result of progressive enolization but the ratios between the quantities of reagent consumed and gas evolved show that in these cases addition to carbonyl is far more rapid than enolization. It seems quite as probable therefore that the sodium compound is formed by addition of sodium alcoholate and elimination of alcohol.

Acetanilide and benzyl benzamide behave exactly like benzhydrol and diphenylamine; the liberated gas is equivalent to the reagent consumed.

⁷ Wislicenus, *Ann.*, 308, 247 (1899).

The resulting magnesium compounds are, doubtless, derived from the enolic modifications.

The last four substances constitute an interesting series. Acetophenone, however carefully dried and purified, always gives at least ten times as much gas as is normally obtained from substances which contain no active hydrogen, but the total amount of reagent consumed is one mole per mole of ketone. Phenyl acetophenone and diphenyl acetophenone also yield an excessive quantity of gas, the former three times, the latter five times the normal amount. In acetomesitylene, finally, the liberated gas is equivalent to the reagent consumed: one mole per mole of ketone.

The explanation of these peculiar results is as follows. In acetomesitylene the hindrance to addition of the Grignard reagent to the di-ortho substituted carbonyl group is prohibitive; the sole products of the reaction are, therefore, methane and the magnesium derivative $(\text{CH}_3)_2\text{C}_6\text{H}_2\text{C}(\text{OMgI})\text{:CH}_2$. In acetophenone the hindrance is comparatively small but the amount of enolization is still appreciable. The substitution of phenyl for hydrogen in the methyl group of acetophenone has a twofold effect: it increases the hindrance to addition and thereby favors the formation of the metallic derivative, but it also, like the introduction of methyl into dibenzoylmethane, diminishes the tendency to enolize. The result of these opposing influences appears to be a slight diminution in the amount of enolization. The work of Grignard and others⁸ shows that in the reactions between ketones and organic magnesium compounds addition to carbonyl and enolization occur as competing processes far more frequently than we are aware. Grignard and Savard in a recent paper⁹ have described the action of 22 Grignard reagents on pulegone. They obtained the most extensive enolization when the alkyl group was secondary or tertiary and contained 3 or 4 carbon atoms. The series under consideration presents another factor of importance. Here the hindrance to addition is not due to the complexity of the magnesium compounds; it lies in the structure of the ketone and in acetomesitylene it is so great that even the simplest Grignard reagent leads to complete enolization.

Use and Limitations

The foregoing list of compounds was selected from more than a hundred that have been examined, because they are well known, present no complications, and show both the nature of the results and the accuracy attainable. It is evident that the reaction with methyl magnesium iodide can be used for learning much more about the structure and properties of an organic compound than merely the number of active hydrogen atoms it

⁸ (a) Dupont, *Compt. rend.*, 154, 599 (1912); (b) Grignard and Savard, *Bull. soc. chim.*, 35, 1081 (1924).

⁹ Grignard and Savard, *Bull. soc. chim. Belg.*, 36, 97 (1927).

contains. For this reason an examination of its behavior in the new apparatus has in this Laboratory become a part of the systematic investigation of almost every new compound. Such an examination consumes but little time, once the apparatus is set up and charged, because a single charge of reagent serves for more than a hundred determinations. Analyses of the reagent immediately after its preparation and after it had remained in its receptacle, exposed to light for months, show that its composition is invariable. When the apparatus is thus permanently set up it can be used with advantage in all cases in which it is possible to determine active hydrogen by the Zerewitinoff method; but since it is more complicated and more liable to injury than that devised by Zerewitinoff, and also requires more experience for its successful operation, it would not be worth while to construct it merely for the purpose of an occasional determination of active hydrogen.

We have found that while an examination of the behavior of a substance toward methyl magnesium iodide is helpful in many—perhaps most—cases, there are others in which it is quite unprofitable. In some of these the substance is not sufficiently soluble in the reagent, a difficulty which can usually be overcome by first dissolving it in some indifferent solvent. We have used dry xylene which was added to the substance after it had been weighed into the flask. The values marked with an asterisk were obtained in this manner.

A much more frequent complication is due to the formation of insoluble intermediate addition products. These rarely interfere with the determination of active hydrogen, and sometimes disappear on prolonged heating, but not infrequently make it impossible to complete the reaction.

A third difficulty arises from the occurrence of successive reactions. These appear most frequently in cases involving oxidation and reduction, and reveal themselves by a slowly diminishing evolution of gas. In these cases it is impossible to determine when the reaction is complete.

Summary

This paper contains:

1. A description of an apparatus for determining the gas evolved and the reagent consumed in reactions between methyl magnesium iodide and organic compounds.
2. A list of values showing the degree of accuracy obtainable.
3. A discussion intended to indicate the use of the apparatus.

CAMBRIDGE 38, MASSACHUSETTS

ADDITIONS AND CORRECTIONS

1926, VOLUME 48

Reduction Equilibria of Zinc Oxide and Carbon Monoxide, by Charles G. Maier and Oliver C. Ralston.

P. 364. The authors of this paper write as follows: "Dr. Charles Rosenblum of the University of Rochester has kindly called our attention to an error in our paper on 'Reduction Equilibria of Zinc Oxide and Carbon Monoxide' appearing in the JOURNAL, Vol. 48, p. 364, 1926. The value of the T^2 coefficient for ΔC_p in Table III, p. 370, is incorrect because of an algebraic error in the summation and should be -14.73×10^{-7} instead of $+22.47 \times 10^{-7}$. This produces a small change in the value of I , which now becomes -60.305 ± 0.091 , and the standard free energy equation on this basis is $\Delta F^\circ T = +47,390 + 4.467 \ln T - 1.56 \times 10^{-3} T^2 + 2.455 \times 10^{-7} T^3 - 60.305 T$. The free energy of formation of zinc oxide at 298°K. is $-75,720$. Other values depending upon these figures will in consequence be subject to a small correction which, however, in general will be less than the experimental error of the determinations, and well within the figure of 300 calories probable error which we estimated in this work."

1927, VOLUME 49

The Preparation of Crystalline *d*-Talonic Acid, by Oscar F. Hedenburg and Leonard H. Cretcher.

P. 479. In line 7 instead of "gulconic" read "gulonic."

Structure of a Protective Coating of Iron Oxides, by Richard M. Bozorth.

P. 975. The last line of Table V should read, "Thickness of Fe_2O_3 layer, 2×10^{-4} cm.; thickness of Fe_3O_4 layer, 2×10^{-4} cm."

Reciprocal Solubility of the Normal Propyl Ethers of 1,2-Propylene Glycol and Water, by Henry L. Cox, William L. Nelson and Leonard H. Cretcher.

P. 1080. In line 8 instead of "low" read "high."

Fluorescein and Some of its Derivatives, by W. R. Orndorff and A. J. Hemmer.

P. 1277. Table I. In the first line of data, Col. 3, instead of " $\text{F} + 2\text{CH}_3\text{OH}$," read " $\text{F} + \text{CH}_3\text{OH}$."

In the seventh line of data, Col. 3, instead of " $\text{F} + 2\text{CH}_3\text{CO}$," read " $\text{F} + \text{CH}_3\text{COOH}$," Cols. 7 and 8, instead of " CH_3CO ," read " CH_3COOH ."

In the eighth line of data, Col. 3, instead of " $1\text{CH}_3\text{CO}$," read " CH_3COOH ."

In the sixteenth line of data, Col. 3, instead of " $\text{F} + 2\text{C}_6\text{H}_5\text{NO}_2$," read " $\text{F} + \text{C}_6\text{H}_5\text{NO}_2$."

P. 1278. Table II. In the third line of note *b*, instead of "This carbonate . . .," read "This carbamate . . ."

The Composition of Corn Wax, by R. L. Shriner, F. P. Nabenhauer and R. J. Anderson.

P. 1291. Last paragraph. "CORRECTION.—The credit for supplying the acids used for comparison by Dr. R. L. Shriner should be given to others. The behenic acid was prepared by Dr. R. R. McGregor and the *n*-eicosanoic acid was a synthetic product prepared by Dr. J. R. Johnson.

CARL R. NOLLER."

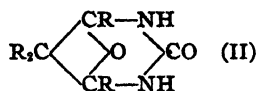
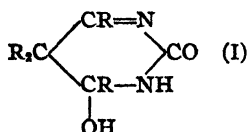
Researches on Thiazoles. II. The Nitration and Reduction of 2-Mercapto-benzothiazole and its Substituted Derivatives, by Jan Teppema and L. B. Sebrell.

P. 1779. Third paragraph, second line, instead of "6-phenyl-2-mercaptobenzo-thiazole," read "6-nitro-2-phenylbenzothiazole."

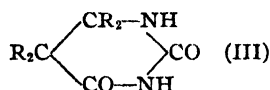
Action of the Grignard Reagent on Alkylbarbituric Acids, by Arthur W. Dox.

P. 2275. Addendum supplied by the author as follows:

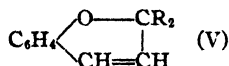
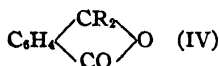
In a recent paper of the above title¹ the writer showed that 5,5-dialkylbarbituric acids react with the Grignard reagent to form stable crystalline products. In the case of diethylbarbituric acid and ethylmagnesium bromide a complete analysis of the product gave the empirical formula $C_{12}H_{22}O_2N_2$. With barbituric acids or Grignard reagent containing other alkyls the nitrogen determinations indicated analogous products. The formula represents a product which would result from a reaction between one mole of the barbituric acid and two moles of Grignard reagent with loss of one molecule of water. On the assumption that two carbonyls had reacted and that the water could be split out in either of two ways, two structural formulas were tentatively proposed:



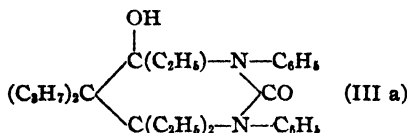
A third possibility occurred to the writer at the time but was not mentioned because it seemed less in conformity to the usual Grignard reactions. This consists in the reaction between a single carbonyl and two molecules of Grignard reagent with loss of one molecule of water, giving a product (III) with the same empirical formula:



It now appears that precedent is to be found for reaction products of Type III, since anhydrides and lactones react in this manner. Bauer² obtained dialkylphthalides (IV) and Houben³ dialkylchromenes (V) by reaction between a single carbonyl and two molecules of Grignard reagent.



In the case of 1,3-diphenyl-5,5-dipropylbarbituric acid, where three Grignard reagent molecules reacted and one molecule of water was split off, the product, if represented by Type III, would be



The constitution of these substances still remains to be determined, but in the light of Bauer's and Houben's work Type III affords a fairly satisfactory explanation of the reaction except that hydrolysis would be expected to yield an amine instead of the ketone actually obtained.

ARTHUR W. DOX

Magnesium Diethyl and its Reaction with Acetyl Chloride, by Henry Gilman and F. Schulze.

P. 2329. In lines 9 and 18-19 instead of "dimethylethylcarbinol" read "methyl-diethylcarbinol."

¹ Dox, *THIS JOURNAL*, **49**, 2275 (1927).

² Bauer, *Ber.*, **37**, 735 (1904).

³ Houben, *Ber.*, **37**, 489 (1904).

NEW BOOKS

A System of Qualitative Analysis for the Rare Elements. By ARTHUR A. NOYES and WILLIAM C. BRAY. The Macmillan Company, New York City, 1927. 536 pp. 22 × 14.5 cm. Price, \$5.00.

Widespread use, to say nothing of imitations more or less shameless, has attested, for thirty years, the value of A. A. Noyes' *Qualitative Chemical Analysis*. From time to time outlines of a more comprehensive system have appeared in various periodicals and as communications to various societies. Now we have a finished masterpiece which insures to its authors long-continued preëminence in the qualitative field, as well as considerable influence upon the quantitative procedure of the future. The contributions of twenty-nine collaborators, distributed over the long period of development of the book, are duly acknowledged.

"Qualitative Analysis for the Metallic Elements" might describe the contents more exactly, as practically all are included—even hafnium separated from zirconium. The rare earth group is to a large extent resolved, and the balance of the fractionations indicated by references. The fact that whole pleiads are detected along with thallium, lead, thorium, bismuth and uranium should be emphasized. Acid radicals are not included, except some containing metallic elements. Incidentally it appears that a comprehensive system for detection of acid radicals constitutes a new world for conquest.

The "Confirmatory Experiments," two hundred pages crammed with experiments and references, afford reading of absorbing interest, and form in many respects the most valuable feature of the book. As the authors remark, this material, if presented in the discursive manner customary in periodicals, would fill a bulky volume. Lastly come "Reactions of the Elements" in tabular form, the first really satisfactory summary of the kind that the reviewer has seen.

The authors tend to diverge sharply from traditional procedures and to introduce striking novelties, such as ethyl acetate as extracting agent or solvent, or the free use of concentrated perchloric acid alone or with hydrobromic, formic or other acids. As reagents for the alkali group we find the unfamiliar sequence: magnesium uranyl acetate, sodium bismuthinitrite, antimony trichloride, sodium hydrotartrate or 6-chloro-5-nitrotoluenemetasulfonate, and silicotungstic acid. Only a study of the confirmatory experiments can show how great are the economies of time and effort, as well as the safeguards against error, gained by the analyst who will restock his reagent shelves.

A modern introductory chemical course consisting mainly of diluted physical chemistry, followed by the usual half year of "qualitative" will afford very scanty preparation for the task set by Noyes and Bray. While we cannot return to the days when the majority of chemists had a really

minute knowledge of inorganic properties and reactions, it is a pity to see the breed so nearly extinct as it is at present. Who knows but that its partial regeneration may be one of the good effects of this remarkable book?

G. S. FORBES

Outlines of Theoretical Chemistry. BY FREDERICK H. GETMAN, Ph.D., formerly Associate Professor of Chemistry in Bryn Mawr College. Fourth edition, revised and partly rewritten. John Wiley and Sons, Inc., New York City, 1927. xii + 728 pp. 179 figs. 22 × 14.5 cm. Price \$3.75.

In the preface of the first edition, the author stated: "The book is designed to meet the requirements of classes beginning the study of theoretical or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject. . . . With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments. . . . In selecting material for this book, the author has been guided in a large measure by his own experience in teaching theoretical chemistry to beginners and to advanced students. . . . While the treatment of each topic is brief, effort has been made to avoid the sacrifice of clearness to brevity."

The latest edition of "Outlines of Theoretical Chemistry" is about 250 pages larger than the first edition, which appeared in 1913, and 100 pages larger than the preceding edition. The book underwent a drastic revision and extensive remodeling in the second edition (1918); and was again brought up to date in 1922, when much new material, including the results of recent work on atomic structure, was included. In the latest edition, "Outlines of Theoretical Chemistry" has once more been revised and extended, but in order to prevent it from becoming too voluminous, certain sections have been deleted or greatly abbreviated.

The arrangement of the book is that of many introductory works on this subject. The chapter headings are: Fundamental Principles; Gases; Liquids; Solids; Relation between Physical Properties and Molecular Constitution; Elementary Principles of Thermodynamics; Solutions; Dilute Solutions and Osmotic Pressure; Solutions of Electrolytes; Colloids; Thermochemistry; Homogeneous Equilibrium; Heterogeneous Equilibrium; Chemical Kinetics; Electrical Conductance; Electrolytic Equilibrium and Hydrolysis; Electromotive Force; Electrolysis and Polarization; Photochemistry; Electrical Theory of Matter; Radioactivity; Atomic Structure. The chapters on chemical kinetics, colloids and photosynthesis are particularly good, and the chapter on thermodynamics has been much improved.

"Outlines of Theoretical Chemistry" has steadily improved with each edition. It is carefully and well written and Dr. Getman is to be commended for the clear, concise and simple manner in which he introduces the beginner to the theoretical side of chemistry. An admirable feature is the numerous and well-selected problems which are placed at the end of most of the chapters for the purpose of testing the student's mastery of the subject matter of the chapter. In the opinion of the reviewer, this book is one of the outstanding introductory texts on the subject.

Necessarily, some of the topics are treated very briefly and therefore superficially—a fault which it would be difficult to avoid in a book of the scope of "Outlines of Theoretical Chemistry." Perhaps, however, half a loaf is better than no bread, especially as the student is enabled to round out and to expand the topics presented by means of the numerous references to original papers, and the list of authoritative books given at the end of each chapter.

The reviewer feels that the section on the activity concept is too meager in view of the large amount of investigation that has been carried out in this field during the past decade, and that Debye and Hückel's theory of solutions of strong electrolytes might have been presented somewhat more fully. In the opinion of the reviewer, it is unfortunate that, like so many writers, the author is not consistent in the use of prefixes, and that he employs the hybridism "unitrivalent." Being human, the author has allowed a few misprints to remain in the text, but most of these are obvious. There are, however, a few cross references to pages in the preceding edition of the book. From experience, the reviewer appreciates the difficulty of preventing this. These, however, are but minor defects in a book which contains a wealth of excellent, thoroughly serviceable, well-arranged and well-selected material.

Dr. Getman is to be congratulated on the continued success of his "Outlines of Theoretical Chemistry." The improved new edition is certain of a cordial welcome from its many old friends. To them it requires no recommendation; to others it can be warmly commended as an introduction to the study of theoretical chemistry.

The mechanical execution of the book is excellent.

H. JERMAIN CREIGHTON

Müller-Pouillet's Lehrbuch der Physik. 11. Auflage, Dritter Band, Zweite Hälfte. Kinetische Theorie der Wärme. By KARL F. HERZFELD, München, unter Mitwirkung von H. G. Grimm, Würzburg. Friedr. Vieweg und Sohn Akt.-Ges., Braunschweig, 1925. 436 pp. 52 figs. 25.5 × 17 cm.

The present volume is not an older edition circumspectly patched and sprinkled with recent references. It is, for the most part, a brand new production aiming to develop the applications of the kinetic theory

and to enlarge the circle of those who can use it with facility. The author, recently transplanted from Munich to Baltimore, emphasizes his desire to make clear the physical content of every statistical formula, as well as that of the corresponding thermodynamical formula, without presupposing unusual mathematical ability upon the part of his readers.

Starting with elementary and familiar considerations, theorems and equations in their first approximations are developed—"learning put lightly, like powder in jam." Next come "Verfeinerung der Betrachtung," "Exkurs," "genauere Diskussion," also footnotes and paragraphs in fine print to tempt the reader further. Through the references, only, would the limits of modern speculation be reached. The author with all his erudition is now primarily a teacher, again almost a propagandist, but a pedant never. In such fashion he treats kinetic theory of gases (elementary presentation), general statistical mechanics (postponing, however, Liouville's theorem and the ergodic hypothesis), gases, liquids, solids, solutions, disperse systems, quantum theory, advanced statistical discussion. Only at the very end come the numerical values, and this is the only feature at which the chemist might cavil.

Such a work is peculiarly helpful to those who cannot "take a course" and so have to dig things out for themselves; to the doctoral candidate in those last desperate hours before his "oral;" or—publish it not—to the lecturer on physical chemistry in the last moments before he meets his class. The trend of modern chemistry in many of its aspects is so obviously toward the kinetic and the statistical, that Herzfeld's book, supplemented perhaps by Tolman's Statistical Mechanics, will be welcomed by all those who read aright the signs of the times.

G. S. FORBES

Optische Methoden der Chemie. (Methods of Photochemistry.) By FRITZ WEIGERT, Professor at the University, Leipzig. Akademische Verlagsgesellschaft m. b. H., Leipzig, 1927. xvi + 632 pp. 341 figs. 24 × 16 cm. Price, unbound, M. 36; bound, M. 38.

For nearly a quarter of a century Weigert has been an indefatigable contributor to the periodical literature of photochemistry. Now the sum total of his experience, backed by intimate knowledge of the work of his contemporaries, has been applied to the production of a book certain to prove of great value to all who contend with the difficulties and exasperations peculiar to the subject.

All the important topics, with numerous ramifications, are included: optical instruments, light sources, ray filters, photographic operations, spectroscopy, photometry, spectrophotometry, colorimetry, nephelometry, measurement of color, radiometry, photochemical measurements (in the special sense), refraction, polarized light, scattered light, luminescence.

The author's sound and practical discussion is more frequently concerned with general principles than with the details of special procedures. He succeeds in giving, throughout, distinctly more than orientation and introduction, and much of the material included could scarcely be found elsewhere. The quantitative point of view predominates. A thousand references, more or less, direct the reader further without adding unreasonably to the thickness and price of the book. These references are commendably up to date, and include a great deal of non-German research. In the reviewer's opinion a considerable expansion of the list would be justified; eight brief citations, for instance, scarcely do justice to the achievements of Coblenz.

Those who have the will to turn out research of permanent value can go far with the help of this book. The semi-quantitative photochemist—may his tribe decrease—will find here both the incentive and the path to reform.

G. S. FORBES

Phosphoric Acid, Phosphates, and Phosphatic Fertilizers. By WM. H. WAGGAMAN, Scientist in Fertilizer Investigations, Bureau of Soils, U. S. Department of Agriculture, assisted by Henry W. Easterwood, formerly Chemist, Bureau of Soils, U. S. Department of Agriculture American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, at 29th Street, New York City, 1927. 370 pp. 58 figs. 15.5 X 23.5 cm. Price \$7.50.

This monograph brings together in convenient form a great deal of information—chemical, economic and technologic—with reference to phosphoric acid, phosphates and phosphatic fertilizers. The introductory chapter is a long one, including a variety of topics such as a brief review of the elementary chemistry of phosphorus; the role of phosphorus in life processes; the phosphorus requirement of soils; naturally occurring phosphates, etc. Chapter 2 deals with phosphate deposits in the United States, and Chapter 3 with phosphate deposits in foreign countries. Chapter 4 deals with so-called available phosphates, while those which are water-soluble are discussed in Chapter 5. Chapter 6 is devoted to a discussion of the sulfuric acid method of preparing phosphoric acid, while Chapter 7 is concerned with the volatilization process of preparing phosphorus and phosphoric acid. Chapter 8 deals with phosphate baking acids and powders; Chapter 9 with the use of phosphates as water softeners, and Chapter 10—the final chapter—with miscellaneous uses of phosphoric acid. Forty-three pages at the end of the book are devoted to a digest of the United States patents covering processes for the production of soluble and available phosphates by various methods.

A monograph of this sort should be judged as a whole and from this standpoint we believe that the authors have produced a book of considerable merit. Criticism of the book can be made only in a limited number of

specific instances which do not detract from its value as a whole. To the present reviewer there seems to be a lack of balance in certain of the parts and certain instances of poor judgment in choosing illustrations. For example, we may point out that the Liljenroth Process is dismissed with less than half a page, whereas a considerable number of pages are devoted to describing and discussing the experimental unit which was set up and operated at Arlington Farms. With regard to illustrations, we suggest that those on pages 64, 111, and particularly the one on page 243, might well be omitted.

While not up to the standard of some of the monographs in the American Chemical Society Series, we believe that the present one falls well within the average and that the authors are to be congratulated on its production.

HARRY A. CURTIS

Contemporary Developments in Chemistry. Lectures by Eminent Chemists. Columbia University Press, New York, 1927. 464 pp. Illustrated. 23.5 × 16 cm. Price \$11.00.

This is a collection of twenty-five lectures delivered at Columbia University in a special course given during the Summer Session of 1926, on the occasion of the opening of the Chandler Laboratories. The subjects of the lectures and the names of the lecturers are as follows:

Synthetic Organic Chemistry in the Study of Odorous Compounds, by Marston T. Bogert; Chemical Reactivity, by James F. Norris; Chemical Relationships of Sugars, Optically Active Amino Acids, Hydroxy Acids and Halogen Acids, by Phoebus A. Levene; Reversible Oxidation-Reduction Reactions in Organic Systems, by W. Mansfield Clark; Crystal Structure in its Relation to Chemical Problems, by Ralph W. G. Wyckoff; Catalysis and the Mechanism of Chemical Reactions, by Hugh S. Taylor; Carbohydrates, by Sir James Colquhoun Irvine; Oxidative Catalysis in the Body, by Edward C. Kendall; Immunology as a Branch of Chemistry, by H. Gideon Wells; Rare Gases of the Atmosphere, by Richard B. Moore; Synthetic Organic Chemistry, by E. Emmet Reid; Permeability and Electric Phenomena in Membranes, by Leonor Michaelis; Radicals as Chemical Individuals, by Charles A. Kraus; The Influence of Pressure upon Chemical Transformations, by Ernst Cohen; A Development in the Chemistry of Sanitation, by John Arthur Wilson; The Direct Measurement of Osmotic Pressure, by J. C. W. Frazer; Chemistry of Bacteria, by Treat B. Johnson; Contact Catalysis, by Wilder D. Bancroft; Water-Soluble Vitamins, by Elmer V. McCollum; Quantitative Research in the Chemistry of Nutrition, by Henry C. Sherman; Theory of Velocity of Ionic Reactions, by J. N. Brönsted; Physico-Chemical Principles in Electro-Metallurgical Research, by Colin G. Fink; Reactions in Liquid Ammonia, by E. C. Franklin; Agricultural Chemistry,

by Charles A. Browne; Completing the Periodic Table, by B. S. Hopkins.

The lectures, as a rule, are summaries of recent work in their respective fields in which the lecturer himself usually has been a productive investigator. Though presented in this way by specialists, they are nevertheless directed to the general chemical reader rather than to fellow specialists in the field. Such summaries are most useful and are all too rare. This collection is therefore a valuable addition to our chemical literature.

ARTHUR B. LAMB

Elementary Organic Chemistry. By LOUIS A. OLNEY, Sc.D., Professor of Chemistry and Dyeing, Lowell Textile School. Howes Publishing Company, 90 William Street, New York City, 1927. 191 pp. 4 figs. 14.5 × 20.5 cm. Price \$3.00.

"The author has found the publication of this book on Elementary Organic Chemistry necessary because up to the present time no other book has been published which fulfills the requirement of certain classes of students in the Lowell Textile School."

"Between the ten to twenty pages treating the subject of carbon compounds, which is inserted in most modern text-books on General Chemistry, and the three to five hundred page book on the subject, there appears to be no published text which gives the fundamental principles of Organic Chemistry, and a general discussion of the subject, in a space that would correspond to from fifteen to twenty lectures."

A careful reading of the text convinces the reviewer that it is unfortunate for a scientist to be forced in this way to write a text-book on a subject with which he is apparently not directly familiar. This is all the more serious since the users of short texts of this kind will usually not be specialists who are capable of correcting the mistakes.

In addition to many minor mistakes some of the more serious are the constant treatment of esterification as the "exact" equivalent of neutralization, the confusion of hydrolysis and dissociation and the discussion of the basic character of the hydroxyl group in the carboxyl group. A large number of errors in important formulas are apparently typographical but none the less dangerous. Among these are those of propylene, acetylene, diazonium salts and magenta.

No mention is made of such important and simple subjects as synthetic methanol, oxyacetylene cutting of steel and the air-oxidation of naphthalene.

The use of a bulb condenser in fractional distillation, as shown on p. 179, is hardly to be recommended.

In conclusion the reviewer would urge the recognition of a place for a short organic text to fill the needs of students who require only the barest smattering of the subject.

FRANK C. WHITMORE

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biological Procedure.)
Abt. III, Physikalisch-chemische Methoden, Teil B, Heft 3. Edited by Prof. DR.
EMIL ABDERHALDEN. Urban and Schwarzenberg, Berlin N 24, Friedrichstrasse
105 B, 1926. Pp. 385-594. 65 figs. 25.5 × 17.5 cm. Price, M. 9.30.

This is the first "Lieferung" of the volume of Abderhalden's handbook which deals with the methods of colloid research. It contains five articles as follows: Coagulation of Sols and Determination of the Isoelectric Point, by E. Bloch; Methods of Determining Adsorption, by H. Fodor; Methods of Biological Dispersoid Analysis, by V. von Hahn; Determination of the Structure of the Colloidal Micelle, by R. Riwlín; and Ultrafiltration and Electro-ultrafiltration, by H. Bechhold. The article on coagulation of sols deals for the most part with the action of electrolytes on sols, mutual precipitation of sols and the methods of determining the degree of coagulation. The methods described for determining the so-called isoelectric point are; cataphoresis, coagulation, measurement of the displacement of P_H by the addition of an acid or base, osmotic pressure, swelling and viscosity. The section on adsorption gives numerous examples of adsorption of gases and adsorption from solutions both dilute and quite concentrated, chiefly with carbon as adsorbent. The significance of $1/n$ in the Freundlich adsorption equation is discussed and a section is devoted to negative adsorption. The methods of dispersoid analysis discussed by von Hahn are filtration, diffusion, sedimentation, optical methods, coagulation and special methods. The chapter on the composition of the micelle gives chiefly the views of Pauli and Fodor on hydrous ferric oxide and albumin and of McBain on the soaps. Bechhold's chapter naturally deals primarily with his own work on ultrafiltration.

The articles in this volume give what appears to be a fairly comprehensive survey of the investigations of Europeans, especially the Germans, in the subject under discussion. Almost no attention is paid to American work. The important question of ionic antagonism in biological systems is passed over in a sentence, page 396, and in all the discussion of adsorption by charcoal there is no reference to the work of Coolidge or of Bartell and Miller on ash-free charcoals. Thirty pages (547-577) are devoted to the physical chemistry of the proteins but there is no reference to Loeb although his investigations doubtless furnished the inspiration for much of the work reported in this section.

HARRY B. WEISER

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PROCEEDINGS

OF THE

American Chemical Society

1927

EASTON, PA.
MACK PRINTING COMPANY
1927

Proceedings

DIRECTORS' MINUTES

The Directors of the AMERICAN CHEMICAL SOCIETY met at the Chemists' Club, New York City, on November 27, 1926, at 3 P. M., with President James F. Norris in the chair and Directors Bancroft, Bigelow, Talbot, Teeple and Parsons present.

John E. Teeple was re-elected Treasurer for a period of three years.

The Secretary announced the gift of Five Thousand Dollars from the Chemical Foundation to enable the Industrial Journal to print without delay the accumulated and important manuscripts on hand. The Industrial Journal had accepted manuscripts to fill its pages until June, some of them of unusual importance to the chemical industries. The gift of Five Thousand Dollars will enable this JOURNAL to print all, except the manuscripts now on hand, not later than the February issue. The Directors approved the action of the Secretary and Business Manager in accepting the gift on their behalf and requested him to send their appreciative thanks to the Chemical Foundation and to Mr. Francis P. Garvan.

The Directors considered the advisability of holding an exhibit of chemical manufacturers, chemical apparatus, chemical books, etc., at each annual meeting of the SOCIETY at the risk and for the financial benefit of the general Society. In view of the success of the exhibit at Philadelphia and the success of similar exhibits by other organizations, the Directors referred the question of holding such an exhibit at our annual meeting to the business manager with power.

It was voted that \$500 be added to the salary of E. J. Craue and for the present that this addition be charged to the budget of the Second Decennial Index.

The following budget was then adopted:¹

ESTIMATED INCOME

	Budget 1926	Budget 1927
Dues.....	\$190,000.00	\$195,000.00
Subscriptions.....	26,000.00	29,000.00
Back Numbers.....	5,000.00	5,000.00
Reprints.....	3,000.00	4,000.00
Postage.....	5,000.00	5,500.00
Interest.....	6,000.00	8,000.00
Advertising.....	105,000.00	107,500.00
Monographs Royalties.		780.00
	<hr/> \$340,000.00	<hr/> \$354,780.00

EXPENDITURES

Journal American Chemical Society.....	49,728.00	\$ 51,334.00
Chemical Abstracts.....	103,000.00	107,900.00
Industrial and Engineering Chemistry.....	75,413.00	78,240.00
News Edition.....	12,805.00	13,145.00
News Service.....	8,500.00	8,550.00

¹ Any member desiring or requiring fuller detailed information regarding any item can obtain it by communicating with the Secretary.

Secretary's Office:

Secretarial.....	10,350.00	10,350.00
Business Management.....	14,450.00	15,450.00
Treasurer's Office.....	3,500.00	4,850.00
President's Office.....	1,200.00	1,200.00
Printing Reprints.....	7,500.00	7,750.00
Advertisements, Printing and Development.....	36,560.00	37,875.00
Scientific Monographs.....	1,060.00	1,060.00
Technologic Monographs.....	25.00	1,025.00
Table of Physical Constants.....	500.00	500.00
Back Numbers.....	4,000.00	4,000.00
Local Sections.....	11,000.00	11,000.00
Incidentals.....	1,500.00	1,500.00
General Meetings.....	2,500.00	2,500.00
Metric System.....	100.00	100.00
Directory, 1927.....		4,300.00
	<hr/>	<hr/>
	\$343,691.00	\$362,629.00

CHARLES L. PARSONS, *Secretary*

COUNCIL

The following communication was sent to the Council on November 26, 1926:

AMERICAN CHEMICAL SOCIETY

Council of the American Chemical Society:

GENTLEMEN:

The following members have been nominated for the offices indicated for the years 1927 and 1927-1929. Kindly check your choice with an X and return in the inclosed ballot envelope. Ballot is void unless received on or before December 16, 1926.

By vote of the Council the names are arranged in alphabetical order.

Yours very truly,

CHARLES L. PARSONS, *Secretary*

President: 1927 only (one to be chosen) (alphabetically arranged): C. A. Browne, Irving Langmuir, S. W. Parr, George D. Rosengarten.

Directors: 1927-1929, inclusive. Nominees of local sections (alphabetically arranged). Vote for one Director in each of the following two geographical districts:

First District: (Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut and Canada), Charles A. Kraus, James F. Norris, H. P. Talbot. *Third District:* (Pennsylvania, Delaware and Ohio), A. C. Fieldner, Charles L. Reese.

Councilors-at-Large: 1927-1929, inclusive (four to be chosen). (Ballot is void unless four are voted for) (alphabetically arranged): Edward Bartow, C. A. Browne, H. N. Holmes, S. C. Lind, H. S. Miner, R. B. Moore, Hugh S. Taylor, Gerald L. Wendt.

The returns of this ballot were counted on December 16 by a committee consisting of W. D. Collins, W. W. Skinner and Charles L. Parsons, and the following officers were elected:

President: George D. Rosengarten.

Directors: James F. Norris, Charles L. Reese.

Councilors-at-Large: Edward Bartow, C. A. Browne, S. C. Lind, H. S. Miner.

CHARLES L. PARSONS, *Secretary*

On recommendation of the Editor in Chief of the Journal of Physical Chemistry, Professor Harry B. Weiser and Professor John Johnston have been appointed Associate

Editors of the Journal of Physical Chemistry by action of the Executive Committee. They replace Arthur L. Day and W. Lash Miller whose terms expire on December 31, 1926.

MEMBERS ELECTED BETWEEN NOVEMBER 15 AND DECEMBER 15, 1926

AKRON SECTION

Bowers, John L.

AMES SECTION

Byrkit, Rollin J.
Catlin, Willard
Craig, Frederick S.
Emmert, Emery M.
Fothergill, Robert E.
Harlan, William R.
Hsieh, T. Y.
Leifson, Einar
McGlumphy, Jas. H.
Meints, R. E.
Peterson, W. D.
Taylor, Milton W.
Vernon, Clarence C.

ARIZONA SECTION

Van Horne, Don

CALIFORNIA SECTION

Harms, Theodore F.

CENTRAL PENNSYLVANIA SECTION

Bartlett, Perry G.
Hinnershitz, Elmer F.
Holtzinger, A. H.
Hoynak, P. X.
McCabe, William A.

CHICAGO SECTION

Ball, C. Olin
Bond, Henry R., Jr.
Brinker, Howard C.
Christopher, Edward F.
Dennis, C. C.
Eakins, John F.
Embree, H. C.
Gill, Mignon
Guisberg, Bernard
Hammer, Inez
Hough, Inez
King, A. E.
Lavalie, Vern G.
Marsh, Geo. Everett
Naef, Ulrich G.
Ritchie, A. V.
Rockwood, Benjamin Newton
Suthard, James

CINCINNATI SECTION

Coughlin, Francis J.
Halberstadt, G. Thomas
Jensen, Harold S.
Jewett, Ernest E.
Krautz, Rudolph W.
Osterhof, Arthur L.
Pagnucco, John Wm.

Rankin, W. P.
Shirk, Loren H.
Skogstrom, J. A.
Votaw, Verling
Weber, Orval G.
Weigand, Sylvester A.

CLEVELAND SECTION

Cain, D. J.
Laubmann, Richard M.
Lee, Charles F.
Poffenberger, Noland
Rose, Bernard L.

COLORADO SECTION

Bahret, Wm. H., Jr.
Berchet, Gerard J.
Continental Oil Company
Katz, M. M.
Mills, Glenn E.

CONNECTICUT VALLEY SECTION

Bruce, William F.
Farrar, George E., Jr.
Flood, Donald T.
Fowler, George B.

DELAWARE SECTION

Lynch, Cecil C., Jr.
Rupert, William S.
Thomaschewski, Dr. Paul E.
Weedon, Wm. Stone

DETROIT SECTION

Lyons, Edward
Segal, David

ERIE SECTION

Galmish, Gilbert L.

FORT WAYNE SECTION

Forsythe, Owen
Leigh, Edwin

ILLINOIS-IOWA SECTION

Burgston, C. H.

INDIANA SECTION

Cox, Amon
Metcalf, Harold B.
Zetterberg, Edward

IOWA SECTION

Goergen, Sylvia M.
Morrison, Dempsey B.

KANSAS CITY SECTION

Maurer, Arthur Binnette
Small, Sanford W.
Warren, Gordon G.

LEHIGH VALLEY SECTION

Bowman, Paul E.
 Bunce, Earl H.
 Curts, Robert M.
 Schaeffer, Harry J.

LEXINGTON SECTION

Cleveland, Forrest
 Veler, Clement D.

LOUISIANA SECTION

Gerstner, Henry George

MAINE SECTION

Huestis, Charles S.

MARYLAND SECTION

Day, Lester E.
 Dunning, Fitzgerald
 Marriott, Maj. C. L.
 Newcomb, Eric McGee
 Rush, R. I.
 Taylor, Roger Kirkbride
 Washburne, R. N.

MICHIGAN STATE COLLEGE SECTION

Burdick, Orel Z.
 Spurway, Chas. H.

MINNESOTA SECTION

Vogel, Herbert

NEBRASKA SECTION

Durban, Sebastian A.
 Fluevog, Edwin A.
 Ralston, Robert R.

NEW HAVEN SECTION

Gilman, Elizabeth
 Hoadley, Eugene W.
 Smith, Willfred W.

NEW YORK SECTION

Auwater, George
 Bischoff, Joseph C.
 Bruce, Geo. Howard
 Burgess, Kenneth E.
 Caine, George C.
 Chilean Nitrate of Soda Educational Bureau
 Conlon, John F.
 Crist, Ray H.
 Eagles, R. H.
 Foulk, Martha E.
 Husted, Helen G.
 Kapinkin, Vadim K.
 Kenny, Christopher L.
 Launder, William C.
 Orton, Clayton Roberts
 Pestoff, Alexis
 Schreiber, Milton J.
 Schunckes, Dr. Franz C.
 Sewell, Milton D.
 Siebenschein, Robert

NORTH CAROLINA SECTION

Dabbs, John L.

NORTHEASTERN SECTION

Bigelow, Newell M.
 Bridgess, M. Philbrick
 Fessenden, Richard W.
 Garside, Kenneth G.
 Gee, Warren Herbert
 Hicks, Laurence C.
 Knight, Kenneth H.
 MacMasters, Majel M.
 Norton, Paul L.
 Roberts, Richard S.
 Shaw, Harlan Page
 Stebbins, Henry Dows
 Thomson, George
 Wedlake, George N.

NORTH JERSEY SECTION

Berger, Ernest E.
 Fortin, Thomas P.
 Muller, Julius F.
 Switz, Theodore MacLean
 Walrath, Otto J.

NORTHWEST UTAH SECTION

Gaudin, A. M.

OKLAHOMA SECTION

Allinson, J. J.
 Eastman, Fred T.

PHILADELPHIA SECTION

Atlantic Refining Company
 Baum, Alfred
 Coats, Hal B.
 Earushaw, David P.
 Knoll, Ralph J.

PITTSBURGH SECTION

Dodds, Mary I.
 Roche, James Norman

RHODE ISLAND SECTION

Guild, Ralph Waite
 Parmenter, Ellis F.
 Tinkham, Homer L.

ROCHESTER SECTION

Reed, George H.

ST. LOUIS SECTION

Bohle, Edgar H.
 Landau, Argo E.

SOUTHEAST TEXAS SECTION

Grahame, James Herbert
 Johnson, A. S.

SOUTHERN CALIFORNIA SECTION

Arkin, James A.
 Clark, Donald E.
 Dalton, Robert H.
 Dickerson, Donald L.
 Henderson, Edwin B.
 Koke, Ernest S.

Mead, Carl C.
Osgyan, A.
Scofield, George N.

SYRACUSE SECTION

Klingelhoef, W. C., Jr.

UNIVERSITY OF ILLINOIS SECTION

Copley, M. J.
Sherwood, C. Ray
Wayo, Stephen J.

UNIVERSITY OF MICHIGAN SECTION

Leslie, Robert W.
Roth, Norman G.

UNIVERSITY OF MISSOURI SECTION

Kilburn, Elsie I.

VERMONT

Waldo, Paul V.

VIRGINIA SECTION

Bott, Phyllis A.
Elgin, Joseph Clifton
Hill, William Lee
Scribner, A. K.

WASHINGTON SECTION

Bekkedahl, Norman
Gorman, Lawrence C.
Norton, Raymond John

WISCONSIN SECTION

Chen, S. Y.
Hallett, Lawrence T.
Miller, Lila
Robinson, Rex J.
Zinn, R. E.

NO SECTION

Aono, Takeo
Askam, John Charles
Auten, John T.
Berky, Herbert W.
Cass, Alta
Chesebro, Paul R.
Colgate, M. Evelyn
Considine, Francis Joseph
Drennan, H. E.
Earle, Fontaine Richard
Finley, James A.
Flahault, J. E., Prof.
Fleck, Elmer E.
Fraser, Vincent T.
Goudriaan, Dr. F.
Green, Herbert
Hiraki, Shintaro
Hirsch, Arthur
Jolly, Victor George
Kasai, Fusao
Kauth, Henry J.
Kelly, Chas. Ignatius
Landes, Chester
Langdale, Robert
Matsumura, Konomu
Meisel, James A.
Merriman, Margaret
Mond, Robert Ludwig
Neulon, D. F.
Newton, Clyde J.
Ricketts, Vernon L.
Runkle, L. Leroy
Schofield, Samuel B.
Schott, Marion S.
Smith, Allan K.
Toole, F. J.
Wallace, Kenneth C.
van Zwanenberg, Saal

DECEASED

Blake, Frank C., 2127 Linden St., Wilmington, Del. Died, Nov. 13, 1926.
Hostmann, Jeannot, 115 West 68th St., New York City. Died, Nov. 11, 1926.
Lee, T. Henry, Rio de Janeiro, Brazil. Died, June 1, 1926.
Moore, F. J., Mass. Inst. of Tech., Cambridge, Mass. Died, Nov. 20, 1926.
Morris, J. Lucien, 3264 Altamont Road, Cleveland Heights, O. Died, April 4, 1926.
Smith, A. T., Weston Point, near Runcorn, England. Died, April 1, 1926.
Wellington, Charles, Amherst, Mass. Died, Nov. 15, 1926.

Proceedings

Report of the Secretary of the American Chemical Society for the year 1926

The Society has held two general meetings during the year, one at Tulsa, Oklahoma, April 5 to 9, 1926, and one at Philadelphia, Pennsylvania, September 5 to 11, 1926. The meeting at Tulsa although not confined to any one Division was naturally largely given up to the chemistry of petroleum. It was well attended and was highly successful. The meeting at Philadelphia was the Fiftieth Anniversary Meeting of the American Chemical Society. It was the largest and most important meeting the Society has ever held. It has been fully described in the Society's journals. In connection with it a special Golden Jubilee Number of the American Chemical Society was issued on August 20 as No. 8-A of the Journal of the American Chemical Society. It summarized fifty years of chemistry in the United States and the influence of the American Chemical Society in its development. At this meeting many foreign members and chemists not members were present. The Divisions of the Society gave special programs and special symposia. Fourteen honorary memberships were conferred.

During the year numerous intersectional meetings were held, as has already been announced in the *News Edition*. In addition, the Rubber Division held a special meeting of its own in Akron, Ohio, on February 22 and 23, 1926, and the Cellulose Division and the Paint and Varnish Section also held special and separate meetings in Madison, Wisconsin, on May 28 and 29, 1926. These divisional meetings were successful, and owing to their specific nature were largely attended by the chemists in these branches of industry. The wisdom of encouraging these special division meetings was confirmed. By supplying this special need and demand of our membership greater loyalty to the American Chemical Society was secured. As predicted, this procedure has added interest to the work of the divisions and has enabled them to get together in large numbers for a study of their own special problems.

The membership figures on December 31, 1926, show an increase over those for 1925. The unpaid membership also has shown a distinct decrease. Owing to both of these factors an increased income in 1926 in membership dues of approximately \$10,000 was secured. There was a noteworthy increase also in non-membership subscriptions, but a decrease in the sale of back numbers owing solely to the partial exhaustion of the stock of the Society. The Society has continued to maintain an excellent financial standing for 1926, its income showing a balance over expenditures, as will be indicated in the audit of the Treasurer's report.

The success of the Monograph series still continues, additional monographs having been issued in 1926 with others in press.

Meetings of the Society will be held in 1927 as follows: Week of April 11, Richmond, Virginia; week of September 5, at Detroit, Michigan.

The local sections have continued active, most of them holding monthly meetings throughout the year, with the exception of the summer months. Their programs have been announced and printed in the *News Edition*. One new local section has been added during 1926; namely, the Fort Wayne Section, with headquarters at Fort Wayne, Indiana. One section, the Savannah Section, was discontinued on January 1, 1926.

Membership in the Society on December 31, 1925, was 14,381. On December 31, 1926, it was 14,704. Statistics follow:

Honorary members.....	22
Life members.....	21
Corporation members.....	393
Members paid 1926.....	12,952
Members unpaid 1925 and 1926.....	689
Members unpaid 1926.....	647
	<hr/>
	14,704

The number of members not in arrears registered in the local sections on November 30, 1925, was 10,408. The number on November 30, 1926, was 11,042. The number in each section for 1925 and 1926 is noted below:

Local section	Number of paid mem- bers, 1925	Number of paid mem- bers, 1926	Cash retained from balance 1925	Total receipts 1926
Akron.....	138	167	\$1.75	\$156.25
Alabama.....	37	43	32.60	50.00
Ames.....	55	59	0.00	73.50
Arizona.....	23	30	0.00	50.00
California.....	350	347	0.00	200.00
Central Pennsylvania.....	56	59	0.37	70.00
Central Texas.....	52	52	22.99	22.99
Chicago.....	809	832	0.00	606.75
Cincinnati.....	221	226	0.00	200.00
Cleveland.....	240	256	0.00	200.00
Colorado.....	71	77	4.20	88.75
Columbus.....	105	117	0.43	131.25
Connecticut Valley.....	110	114	0.00	125.00
Cornell.....	58	90	0.08	72.50
Delaware.....	160	173	2.97	152.97
Detroit.....	143	147	0.00	143.00
Eastern New York.....	104	107	0.00	130.00
Erie.....	36	31	1.66	51.66
Florida.....	54	67	0.00	67.50
Fort Wayne.....	..	24	...	20.00
Georgia.....	45	54	4.38	29.38
Hawaiian.....	29	29	44.92	44.92
Illinois-Iowa.....	26	21	0.00	50.00
Indiana.....	137	134	0.00	156.25
Iowa.....	105	96	0.00	131.25
Kansas City.....	146	174	0.00	146.00
Lehigh Valley.....	93	104	0.00	116.25
Lexington.....	30	35	0.00	50.00
Louisiana.....	76	81	0.00	95.00
Louisville.....	27	31	50.00	50.00
Maine.....	35	32	39.08	51.50
Maryland.....	217	239	0.00	162.75
Michigan State College.....	36	36	0.00	54.00
Midland.....	23	24	50.00	50.00
Milwaukee.....	115	111	0.00	143.75
Minnesota.....	186	198	14.27	188.00
Nashville.....	23	22	20.15	50.00
Nebraska.....	26	28	1.98	50.00

Local section	Number of paid mem- bers, 1925	Number of paid mem- bers, 1926	Cash retained from balance 1925	Total receipts 1926
New Haven	107	105	0 00	133 75
New York	1255	1417	29 25	941 25
North Carolina	57	69	17 11	71 25
Northeastern	775	797	0 00	581 25
North Jersey	542	593	0 00	406 50
Northern Louisiana	24	17	0 00	50 00
Northern West Virginia	26	26	15 40	50 00
Northwestern Utah	27	33	4 00	29 00
Oklahoma	74	88	0 63	92 50
Omaha	34	32	0 00	51 00
Oregon	44	40	0 00	66 00
Philadelphia	609	640	0 00	456 75
Pittsburgh	397	430	0 00	290 00
Puget Sound	65	68	42 40	47 25
Purdue	23	30	0 00	50 00
Rhode Island	92	95	0 00	115 00
Rochester	139	155	0 00	156 25
Sacramento	27	27	0 00	50 00
Saint Joseph Valley	22	29	6 79	50 00
Saint Louis	202	216	0 00	200 00
Savannah	16	(Discontinued)		
Southeastern Texas	81	73	9 20	9 20
Southern California	288	301	0 00	216 00
South Jersey	31	35	0 00	50 00
Syracuse	103	106	0 00	128 75
Toledo	40	46	0 00	60 00
University of Illinois	139	121	5 62	156 25
University of Michigan	70	74	0 00	87 50
University of Missouri	31	34	0 00	50 00
Vermont	23	18	10 50	22 80
Virginia	96	97	0 00	75 00
Washington, D C	389	380	0 00	291 75
Western New York	243	237	0 00	200 00
Wisconsin	120	146	37 00	156 25
	10,408	11,042	\$469 73	\$ 9,620 42
Rebates, account new mem- bers secured by local sec- tions				1 555 00
				<u>\$11,175 42</u>

The table gives a summary of the sectional accounts for the year, shows the number of members in each local section for 1925 and 1926, the funds held over from 1925 account, and the total funds (which include the balances) charged to the 1926 account

During the past two fiscal years, December 1, 1924, to November 30, 1926, the Secretary has made the following collections

	1925	1926
Membership	\$188,126 50	\$198,060 00
Subscriptions	26,829 75	29,178 45
Back numbers	6,564 06	5,388 68

Reprints.....	4,029.78	4,576.79
Postage.....	5,109.41	5,443.00
Exchange.....	3.43	4.85
Decennial Index.....	760.00	625.25
Directory.....	261.00	86.00
Interest.....	1,490.81	2,241.99
	\$233,174.74	\$245,554.51

These amounts were duly transmitted to the Treasurer of the Society.

Several sets of *Chemical Abstracts* have been completed and sold during the year as well as complete sets of *Industrial and Engineering Chemistry*. Complete sets of the *JOURNAL* of the American Chemical Society are no longer available as it is impossible to fill in certain early numbers which are exhausted. Nevertheless, the Society has again sold a number of incomplete sets to the extent that they could be completed, and there is still a demand for such, as full sets are unobtainable. The stock has been kept in fair condition by the purchase of numbers needed to complete full volumes. Many volumes are already sold out and a number of other issues of all three of our journals are nearing exhaustion.

Back numbers are mailed direct from Easton, Pa., on orders sent through the Secretary's office. The following is the summary of the back numbers sent out by the Secretary during the year, together with the present stock of journals:

Copies of the Society's publications sent out from January 1, 1926, to December 31, 1926, aside from mailing lists.....	52,557
Copies of the <i>Journal</i> of the American Chemical Society in stock...	13,937
Copies of <i>Chemical Abstracts</i> in stock.....	32,199
Copies of <i>Industrial and Engineering Chemistry</i> in stock.....	16,756
Copies of the General Index, Vols. 1-20, J. A. C. S. in stock.....	58
Copies of the 25th Anniversary Number in stock.....	81
Copies of the Golden Jubilee Number in stock.	4,571
Volumes of First Decennial Index in stock.....	239

Respectfully submitted,
CHARLES L. PARSONS, *Secretary*

Report of the Treasurer

The Auditors' Report presented herewith shows that the Society as a whole, for the year 1926, kept its expenses within the limits laid down by the budget a year ago, while its income was a little larger than predicted a year ago.

The expenses of the Society now amount to about One Thousand Dollars per day, including Sundays, and as long as the income is approximately the same as the expenses we understand that the wishes of the Council and Directors are being followed. We should always remember, however, that this policy leaves us very little reserve, and while we can expand slightly in good years we will be forced to retrench in bad years.

The Officers and Editors who were charged with expending our money on our widely varied activities, have almost without exception, during this last year, kept their expenses just inside of their budget allowance in spite of the many demands made upon them, and the many lines of useful activity where they see that more money could be spent profitably. Probably no one but those intimately acquainted with the financial affairs of the Society realizes quite what an amount of time, thought and experience is required to accomplish this, or what a debt the Society owes to these various Officers and Editors who succeed in getting so much out of the funds at their disposal.

JOHN E. TRIPLE, *Treasurer*

Auditor's Report

New York, January 17, 1927

DR. J. E. TEEPLE, *Chairman Finance Committee*
 American Chemical Society
 50 East 41st Street, New York City

Dear Sir:

Pursuant to your request, we have made an audit of the books of account of the American Chemical Society, kept by its Treasurer, for the year ending December 31, 1926, and submit herewith the accompanying Condensed General Balance Sheet as of December 31, 1926, and Statement of Cash Received and Disbursed between January 1, and December 31, 1926—marked Exhibit "A" and Exhibit "B," respectively, which we have prepared therefrom, and hereby

CERTIFY that such statements correctly reflect the financial condition of the Society at December 31, 1926 and its financial transactions during the year as shown by the books of account.

Yours very truly,

F. W. LAFRENTZ & COMPANY
Certified Public Accountants

AMERICAN CHEMICAL SOCIETY
 CONDENSED GENERAL BALANCE SHEET—DECEMBER 31, 1926

ASSETS

INVESTMENTS:

Trust Funds:

Decennial Index:

\$ 5,500 United States Liberty 1st 4 $\frac{1}{4}$ %, Due 1932-1947....	\$ 5,568.20
12,800 United States Liberty 4th 4 $\frac{1}{4}$ %, Due 1933-1938.....	12,966.68
16,000 United States Liberty 2nd 4 $\frac{1}{4}$ %, Due 1942.....	16,030.40
30,600 United States Liberty 3rd 4 $\frac{1}{4}$ %, Due 1928.....	30,688.74

Total..... \$ 65,254.02

Priestley Memorial—First 5 $\frac{1}{2}$ % Mortgage, Due February 1, 1931— Title Guarantee and Trust Company, Mortgagor.....	1,115.75
Life Membership—First 5 $\frac{1}{2}$ % Mortgage, Due February 1, 1931— Title Guarantee and Trust Company, Mortgagor.....	6,235.04
Morris Loeb—First 5 $\frac{1}{2}$ % Mortgage, Due February 1, 1931—Title Guarantee and Trust Company, Mortgagor.....	25,992.25
Endowment—First 5 $\frac{1}{2}$ % Mortgage, Due February 1, 1931—Title Guarantee and Trust Company, Mortgagor.....	29,000.00

Total... \$127,597.06

General:

\$10,000 United States Liberty 4th 4 $\frac{1}{4}$ %, Due 1933-1938 (Registered).....	\$10,000.00
First 5 $\frac{1}{2}$ % Mortgage, Due December 1, 1930—Title Guarantee and Trust Company, Mortgagor.....	60,000.00
First 5 $\frac{1}{2}$ % Mortgage, Due February 1, 1931—Title Guarantee and Trust Com- pany, Mortgagor.....	37,656.96
10 shares Chemical Foundation, Inc., Stock.....	1,000.00

Total..... 108,656.96

OFFICE FURNITURE AND FIXTURES.....	4,772.71
PUBLICATIONS—(Extra Copies for Future Sale).....	8,000.00

CURRENT ASSETS:

Cash on Hand—As per Exhibit "B,"	\$17,446.73
Accounts Receivable—Advertising, etc.....	14,513.27
Total.....	31,960.00

ITEMS IN COURSE OF ADJUSTMENT:

Industrial Journal—Printing Additional Pages.....	2,353.39
TOTAL.....	<u>\$283,340.12</u>

LIABILITIES

TRUST-FUND RESERVES:

Priestley Memorial Fund.....	\$ 1,115.75
Life Membership Fund.....	6,235.04
Morris Loeb Fund.....	25,992.25
Endowment Fund.....	29,000.00
Decennial Index Fund.....	65,254.02
Total.....	\$127,597.06

TRUST-FUND INCOME ACCOUNTS:

Endowment Fund—Interest.....	\$ 877.25
Priestley Memorial—Interest.....	30.26
Total.....	907.51
BALANCE—Being Excess of Assets over Liabilities.....	154,835.55
TOTAL.....	<u>\$283,340.12</u>

THIS IS TO CERTIFY that we have audited the records and books of account of the American Chemical Society, kept by its Treasurer, and have prepared therefrom the foregoing Balance Sheet, which correctly reflects the financial condition of the Society, as at December 31, 1926, as shown by its books of account.

The Cash in Bank was proven by certificate from the depository, and the Securities were confirmed by actual count.

Certified Public Accountants

AMERICAN CHEMICAL SOCIETY

STATEMENT OF CASH RECEIVED AND DISBURSED BETWEEN JANUARY 1, AND DECEMBER 31, 1926

RECEIPTS

CASH ON HAND JANUARY 1, 1926.....	\$ 30,740.91
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DUES AND MEMBERSHIPS:

Membership Dues and Subscriptions.....	\$226,923.45
Life Membership Dues.....	315.00
Total.....	<u>227,238.45</u>

REVENUE FROM PUBLICATIONS:

Advertising.....	\$106,837.07	
Back Numbers.....	5,388.68	
Directories.....	36.00	
Reprints (Secretary's Office).....	4,576.79	
Total.....		116,838.54

INCOME FROM INVESTMENTS, ETC.:

Special Investment Fund.....	\$ 5,196.58	
Life Membership Fund.....	246.40	
Morris Loeb Fund.....	1,151.15	
Priestley Memorial Fund.....	42.26	
Endowment Fund.....	877.25	
General Funds—Interest on Bank Balances.....	2,936.96	
Total.....		10,450.60

DECENNIAL INDEX FUND:

Subscriptions and Contributions.....	\$ 73,542.80	
Interest.....	2,055.96	
Total.....		75,598.76

MISCELLANEOUS:

Payment for Postage, etc.....	\$ 5,447.35	
Monograph Royalties.....	787.68	
Jubilee Number—Gift Chemical Foundation.....	5,203.88	
From Sale of Securities.....	59,249.26	
Profit Sale of Securities.....	4,602.49	
Total.....		75,290.66

TOTAL RECEIPTS.....	\$536,157.92
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DISBURSEMENTS**PUBLICATIONS AND OTHER GENERAL EXPENSES, ETC.:**

Journal of the American Chemical Society.....	\$ 49,513.30	
Chemical Abstracts.....	107,404.10	
Industrial and Engineering Chemistry.....	76,437.78	
News Edition.....	12,695.95	
News Service.....	8,662.18	
Secretary's Office, including Business Management.....	23,621.61	
Treasurer's Office.....	3,318.98	
President's Office.....	796.44	

Printing Reprints:

Industrial Journal.....	\$ 4,540.52	
Journal of the American Chemical Society.....	2,892.73	
News Edition.....	76.12	7,509.37

Printing Advertisements.....	35,712.43
Scientific Monographs—Editor's Salary and Expense.....	1,040.00
Technological Monographs—General Expenses.....	24.53

Table of Physical Constants—Contributions.....	500.00
Back Numbers.....	3,280.40
Incidentals.....	449.60
Local Sections.....	9,150.69
Local Sections Rebates.....	1,555.00
General Meetings.....	995.62
Metric System—Contributions.....	100.00
Life Membership Dues and Postage.....	327.50
Decennial Index—General Expenses, etc.....	9,180.68
Jubilee Number.....	5,203.88
Priestley Memorial—Medal Expenses.....	80.00
Payment to Smithsonian Institute—Interest Received from Morris Loeb Fund Investment.....	1,151.15
Securities Purchased for General and Trust Funds.....	160,000.00
TOTAL DISBURSEMENTS.....	\$518,711.19
BALANCE—Cash on Hand December 31, 1926.....	17,446.73
GRAND TOTAL.....	<u>\$536,157.92</u>

Report of the Editor of the Journal of the American Chemical Society for the Year 1926

The number of articles published by the Journal, and the number of pages devoted to them and to the Proceedings of the Society during the past five years, exclusive of the indexes and the tables of contents, have been as follows:

	Number					Pages				
	1922	1923	1924	1925	1926	1922	1923	1924	1925	1926
Proceedings.....	117	130	112	82	52
Physical and Inorganic.....	191	209	164	195	209	1844	1700	1396	1475	1619
Organic and Biological.....	148	212	203	243	249	1082	1384	1423	1578	1553
Book Reviews.....	47	57	74	63	77	48	66	69	55	70
Total.....						3091	3280	3000	3190	3294

It can be seen from the figures in this table that the average length of articles, exclusive of Notes, was 6.9 pages during the past year as compared with 6.9 pages in 1925, 8.0 pages in 1924 and 7.5 in 1923. It should be appreciated that this high average of compression is only secured at the cost of great effort, both by the Authors and the Editors.

Our total number of pages, including the 55 pages devoted to the indexes, exceeded by 49 pages the 3300 pages allotted in the Budget. This was possible as the result of a somewhat less cost per page for our printing.

The terms of Associate Editors C. L. Alsberg and H. H. Willard expired during the past year, but fortunately both were willing to accept reappointment for an additional term, so that the Society is assured of a continuation of their valuable services.

ARTHUR B. LAMB, *Editor*

Report of the Editor of Chemical Abstracts for 1926

During the past year 29,202 abstracts were published in *Chemical Abstracts*; these covered 3842 pages. For comparison these figures are given below along with corresponding figures for the nine preceding years..

	Year	1917	1918	1919	1920	1921
No. of abstracts.....		15,601	13,357	14,698	18,051	19,476
No. of pages.....		3,470	2,712	3,338	3,826	4,059
	Year	1922	1923	1924	1925	1926
No. of abstracts.....		23,212	24,256	25,607	26,426	29,202
No. of pages.....		4,365	3,924	3,740	3,618	3,842

The figures for pages of abstracts are not directly comparable in all instances because the printing style was changed from leaded to solid composition on June 10, 1923. It is clearly evident, however, that it has been necessary to exert ever increasing pressure for brevity in order to keep pace with the growing chemical literature within the space limitations necessarily imposed. Except for certain foreign patents we have kept pace in 1926

The increase of 2776 abstracts in 1926 over the number published in 1925 does not exactly represent the growth in the literature. This figure is a little large for that purpose because the effort exerted each year to make the current volume as complete a record for the year as possible was intensified during the latter part of 1926 since this year marks the end of a ten-year period. Every author whose work appeared in time is deserving of a place in the Second Decennial Index—that thought was expressed to the abstractors and their response was fine. The increase in number of abstracts during the ten years shown above is not exactly representative of normal literature growth either as recovery from the effects of the World War is involved. During the year immediately preceding the war (1913) 25,971 abstracts were published. In comparing this figure with the 29,202 abstracts published in 1926 it should be borne in mind that the patent literature was covered more thoroughly in 1913 than is now possible.

Of the 29,202 abstracts published last year, 23,103 are abstracts of papers and 6099 are abstracts of patents. The abstracts of papers have averaged 0.142 page in length as compared with 0.144 page in 1925 and 0.150 page in 1924; the abstracts of patents have averaged 0.055 page in length as compared with 0.058 page in 1925 and 0.069 page in 1924. It will always be wise carefully to conserve space, but it will be a good thing for the journal when abstracts can be reasonably lengthened.

The edition has been 14,800 copies per number during the most of 1926.

On October 20, there was published a revised "List of Periodicals Abstracted." The key to library files (225 libraries) and other information supplied are calculated to make as easy as possible the bridging of the gap between abstracts and full papers. The list includes data regarding 1246 periodicals. A copy was sent to each subscriber to *Chemical Abstracts*. Reprints are available.

Now that the second ten-year period (1917–1926) is completed the actual printing of the Second Decennial Index can be started. The compilation work progressed on schedule during 1926 and it was possible on December 31 to send the first of the copy to the printer. The printing contract was awarded in September to the Mack Printing Co. The printing schedule calls for the completion of the two volumes of author index (approximately 2870 pages) in 1927 and the issuing of the three volumes of subject index (approximately 4130 pages) in 1928.

The following editorial changes have occurred during 1926: Brian Mead, who has been capably assisting George L. Clark with the big section on General and Physical Chemistry, had to give up this work because of his departure from Cambridge, where Dr. Clark is located. E. K. Marshall, Jr., took over the section on Physiology early in the year, Andrew Hunter having resigned after long and faithful service and then later Dr. Marshall consented to take charge of the section on Pharmacology also during A. N. Richards' year in Europe; this is the first time that two sections have ever been handled by one man at the same time. F. C. Blanck and H. A. Lepper became editors

of the section on Foods in April, following the resignation of W. D. Bigelow and A. E. Stevenson; Dr. Bigelow had been an assistant editor ever since the beginning of *Chemical Abstracts* in 1907 so that it was a source of special regret to lose him; Mr. Stevenson was an excellent helper.

Other men who have been actively associated with *Chemical Abstracts* as assistant editors during the twenty years since its beginning are G. E. Barton, C. E. Munroe, L. A. Olney and A. H. Sabin. Those still active who have completed ten or more years in this service are Colin G. Fink, Edgar T. Wherry, William T. Hall, Chas. A. Rouiller, Paul E. Howe, Frank P. Underhill, Stanley R. Benedict, Philip B. Hawk, H. Gideon Wells, Alfred N. Richards, R. A. Gortner, Edward Bartow, W. O. Emery, F. M. Rogers and E. Scherubel. The number of abstractors and of assistant editors who were formerly abstractors whose period of service extends over ten years is too large to enumerate here. To all these men and to the many others who have given, or are giving, unselfishly of their time as abstractors or assistant editors, the editor wishes again to voice his gratitude and to express the belief that all who find *Chemical Abstracts* useful will join him in this. The amount of work done in a spirit of service to chemistry by the 300 folks represented below the top line of names on the *Chemical Abstracts* cover is very great.

Statistics for the various sections follow, figures being given for 1925 for comparison:

	1925		1926	
	No. of pages	No. of abstracts	No. of pages	No. of abstracts
Apparatus and Plant Equipment.....	26.9	335	28.4	360
General and Physical Chemistry.....	325.2	2182	347.4	2382
Subatomic Phenomena and Radiochemistry ..	157.7	1177	196.1	1505
Electrochemistry.....	40.9	297	42.9	324
Photography.....	27.9	210	27.5	212
Inorganic Chemistry.....	68.1	330	76.3	363
Analytical Chemistry.....	102.4	666	82.5	558
Mineralogical and Geological Chemistry.....	58.2	586	57.2	637
Metallurgy and Metallography.....	117.0	876	149.7	1029
Organic Chemistry.....	610.8	1923	627.5	2195
Biological Chemistry.....	726.0	5708	731.4	5524
Foods.....	62.8	512	78.3	620
General Industrial Chemistry.....	12.6	166	22.6	263
Water, Sewage and Sanitation.....	39.1	472	51.5	585
Soils, Fertilizers and Agricultural Poisons....	72.5	643	93.4	691
The Fermentation Industries.....	19.9	180	23.0	194
Pharmaceutical Chemistry.....	79.9	600	88.3	662
Acids, Alkalies, Salts and Sundries.....	23.3	262	30.9	298
Glass, Clay Products, Refractories and Enam- eled Metals.....	33.0	263	54.9	456
Cement and Other Building Materials.....	16.8	172	26.9	239
Fuels, Gas, Tar and Coke.....	97.8	734	88.3	867
Petroleum, Lubricants, Asphalt and Wood Products.....	41.4	378	47.8	470
Cellulose and Paper.....	48.1	363	52.6	393
Explosives and Explosions.....	24.3	129	26.7	168
Dyes and Textile Chemistry.....	38.1	486	48.6	601
Paints, Varnishes and Resins.....	30.5	293	31.7	307
Fats, Fatty Oils, Waxes and Soaps.....	30.0	247	40.7	290

Sugar, Starch and Gums.....	36.4	305	43.7	366
Leather and Glue.....	20.2	255	22.5	276
Rubber and Allied Substances.....	36.4	201	46.6	268
<hr/>				
Total, not including patents.....	3024.2	20,951	3285.9	23,103
Patent Abstracts.....	321.8	5,475	339.6	6,099
<hr/>				
	3346.0	26,426	3625.5	29,202
Book Titles.....	27.9	671	43.5	1,036
Headings, blanks and cross references.....	136.4		124.4	

Respectfully submitted,

E. J. CRANE

Report of the Editor of Industrial and Engineering Chemistry for 1926

Industrial and Engineering Chemistry enjoyed one of its busiest years in 1926, publishing 430 contributed articles, 94 editorials, and reviews of 135 scientific books. During the year 1384 pages—64 more than the usual annual volume—were published, the extra number having been made possible by the generosity of the Chemical Foundation, Inc. Following the Philadelphia meeting it became immediately apparent that unless ways could be found to add pages to the number authorized, the results of scientific and industrial work reported in accepted articles might be delayed for several months, with a probable disadvantage to industry as well as to research of a fundamental character. In accord with its policy to do whatever it can to promote the science of chemistry, the Chemical Foundation was able to make an allotment which has been used in the manner indicated.

The articles appearing during the year included many of outstanding value, and special mention may be made of four symposia. These were Future Trends in Industrial and Engineering Chemistry, Lubrication, Progress of the Dye Industry in the United States during the Past Decade and Raw Rubber.

The esteem in which this journal is held throughout the world may be measured by the rapidity with which surplus copies became exhausted, making it necessary for the Society to repurchase in order to have at hand a few complete sets for future needs.

The placement of the table of contents immediately inside the front cover, an innovation with Volume 18, has been much appreciated by the readers and in the make-up of the journal the effort to improve the appearance of the papers, ease of reading, and the conservation of the readers' time has been continued. There has been no change in the policy to devote the maximum percentage of space to articles of permanent value, and we are convinced that this is a policy acceptable to the membership and advantageous to our advertisers.

The News Edition with every issue more firmly establishes its place in the Society's activities. It serves well in conveying items of more than passing interest and offers the best medium through which to promulgate throughout the world the preliminary and final programs of the semiannual meetings.

The advertising pages have shown a very satisfactory volume of business and those of our readers who do not make a practice of examining these pages promptly upon receipt of the journal will find that they have missed much by not making the most of the information which they contain.

Two notable facts are the extent to which our list of nonmember subscribers in all parts of the world shows a gradual but consistent growth, and the extent to which articles first appearing in this journal are reprinted in the scientific, technical, and lay press everywhere. The editor appreciates the compliment thus paid to the authors

whose articles appear in the columns of *Industrial and Engineering Chemistry* and continues to cooperate heartily with all editors who find in these pages material which they consider worthy of reprinting for their own clientele.

The results that are being achieved would be impossible without the great amount of gratuitous service performed by many members of the Society in the interests of prompt and accurate publication. The divisions of the Society have performed valuable service in indicating members accepted as specialists who are willing to review contributed articles. Many men have given of their time to review books and assist in the decision of questions pertaining to modern technology, and wherever we have turned for advice, whether to our formally constituted board of advisors or to interested members of the Society, we have found an appreciated readiness to assist. The men who translate our foreign letters are particularly helpful. Notwithstanding considerable increase in the business of the office, it has been possible to perform the work on schedule time, thanks to the unstinted efforts of a devoted staff.

H. E. HOWE, *Editor*

Report of the Director of the A. C. S. News Service for 1926

The A. C. S. News Service is now well established as a national organization. Not only do representatives of the various press services and of local papers look to this service for abundant copy on the occasion of our semiannual meetings, but not infrequently the service is called upon to obtain opinions on topics of current affairs and to interpret the significant facts in current work as reported. While special efforts are made on the occasion of our meetings, a steady flow of material is maintained throughout the year with a result that must be gratifying to the membership of the Society. An event such as the Semicentennial Meeting calls for much extra effort but this was put forth by the managing editor and his staff, so that only those who are unable to read remained oblivious of the purport and features of the Philadelphia meeting.

The extent to which the material supplied by the A. C. S. News Service is used makes it altogether too expensive to purchase clippings, as was regularly done a few years ago, and today only an occasional purchase is made, covering a short period and merely for the purpose of checking the general results.

Most of the material supplied by the press is based upon papers presented before national meetings, regional meetings, and local sections, and articles appearing in *Industrial and Engineering Chemistry*. Where leading chemists are willing to give views on timely topics, these continue to be of great use to the News Service. The position of the Society is such that all of its activities constitute news, and through the efforts of the A. C. S. News Service chemistry is unquestionably gaining an increasing circle of interested friends.

H. E. HOWE, *Director*

COUNCIL

James F. Norris, just before terminating his office as President of the Society, appointed C. A. Browne, F. G. Cottrell, and H. J. Wheeler, a committee to cooperate with the Organizing Committee of the First International Congress of Soil Science to be held in Washington, D. C., June 13-22, 1927.

Gerald L. Wendt, of Pennsylvania State College, has been unanimously elected by the executive committee editor of *Chemical Reviews* to succeed W. A. Noyes who desired to be relieved from this duty. Dr. Wendt has accepted the editorship.

MEMBERS ELECTED BETWEEN DECEMBER 15, 1926 AND JANUARY 15, 1927

AKRON SECTION

Johnson, D. W.
Krauss, William E.
Torrance, Philip M.

ALABAMA SECTION

Carson, Harry Young

AMES SECTION

Leermakers, John A.

CALIFORNIA SECTION

Bunds, Clifford C.
Gordon, Thomas Lyne
Lawrence, Richard M.
Martin, Geo. H.
Polissar, Milton J.
Ramsperger, Herman Carl
Simons, Arnold W.

CENTRAL PENNSYLVANIA SECTION

Daugherty, Thomas Hill
Robinson Mfg. Co
Ross, Auburn A

CENTRAL TEXAS SECTION

Jackson, Fannie A

CHICAGO SECTION

Becker, Harold A.
Benjamin, Lionel
Bergman, Donald J.
Cesar, Tom
Challis, Frank Egerton
Erickson, E. T.
Greene, Richard D.
Hedberg, James D.
Holmes, Joseph A.
Jacobson, Orin B.
Johnson, Fred O.
Kochs, Herbert W.
Kolb, Merle A.
Layue, Lawrence E.
Layton, Roy F.
Linnell, Robert C.
Lovejoy, Maurice E.
Paulsen, Herbert A.
Rhodes, C. C.
Schwartz, Philip
Seeley, Clarence H.
Sikes, Alfred W.
Tilton, Herbert F.

CINCINNATI SECTION

Alderks, O. H.
Humbaugh, Nelson W.
Milk, Victor
Thompson, J. F., Jr.

CLEVELAND SECTION

Budge, Pasqual M.
Lannert, George H.
Nichols, William Abner, Jr.

Wardell, Chas. H., Jr.
Whitney, Charles E.
Williams, Robert C.

COLORADO SECTION

Hoenemeyer, A. H.

COLUMBUS SECTION

Conaway, Rollin F.
Heckert, Winfield W.

CONNECTICUT VALLEY SECTION

Carlson, George W.
Leaper, Percy Joshua

CORNELL SECTION

Kaltenbacher, Joseph Charles
Pottinger, John James
Schwartz, Anthony M.
Snyder, Solomon Sidney
Summerson, William H.
Ue, C. M.

DELAWARE SECTION

Lulek, Ralph N.
Wade, W. B.

DETROIT SECTION

Garber, C. Zent
Mauritho, Orson L.

EASTERN NEW YORK SECTION

Briggs, Chauncey L.
Hicks, John Francis

GEORGIA SECTION

Alexander, Harvey B.
Archer, Hiram Ethan
Marshall, William Edwin, Jr.
Newberry, Hugh Wagner
Sanford, R. M.
Sweet, Henry

INDIANA SECTION

Caldwell, A. Lee

IOWA SECTION

Grosz, Oliver
Mullins, George M.
Wickert, J. Nelson

KANSAS CITY SECTION

Browning, Howard F.
Kenyon, William Orlin
Longworth, Lewis G.
Malm, Ignace I.
Roote, Paul M.

LEHIGH VALLEY SECTION

Dahl, Louis A.

LOUISVILLE SECTION

Schimpff, G. Weber

MAINE SECTION

Hill, Warren E.
Sullivan, Alphonso Dennis

MARYLAND SECTION

Bellinger, Frederick
Greenberg, Joseph
Herndon, Lee R.
Mitchell, James A.
Scheidegger, J.
Walters, Francis M.
Willoughby, Carl E.

MILWAUKEE SECTION

Phillips, M. J. W.

MINNESOTA SECTION

Kugler, Joseph H.
Haugrud, Parmalee
Schlafke, William

NEBRASKA SECTION

Huffman, J. M.

NEW HAVEN SECTION

Smith, Rodney P.

NEW YORK SECTION

Beatty, Wallace Appleton
Bruckner, Walter H.
Budinoft, Sylvia M.
Caputo, John A.
Clark, Ralph A.
Cohen, Milford H.
Cook, Graham R.
Coryell, Ralph L.
Dawson, John M.
Dirks, Edward Ferdinand
Dornblatt, Albert Julius
Eaton, Cyrus D.
Engelhart, Louis F.
Hammond, Martha B.
Knowles, D. C., Jr.
Howells, Henry P.
Kostelak, Robert
Mahoney, Paul L.
Maibauer, Albert E.
Matheson, A. M.
Mattin, Harry E.
Miller, Edward Hughes
Minton, David M., Jr.
Ogden, Robert B.
Perryman, George
Pickett, Charles F.
Powsner, Louis L.
Preisman, Louis
Strauss, August C.
Tom, Y. G.
Trohn, Sidney K.
Vinson, Carl G.
Wakelee, Loren A.
Winter, Russell P.
Wyckoff, George Hampton

NORTHEASTERN SECTION

Annis, Leonard
Asbury, Willard Carlton
Boeckeler, B. C.
Bragg, Leslie B.
Bush, Theodore Huggins
Carlson, C. L.
Chapman, Wilder A.
Cooper, Charles Milton
Couch, William H.
Cullinan, John F.
Ebersole, Fred
Fahy, John
Harford, Charles Gordon
Hatton, Robert B.
Ho, Yu-Kun
Kildare, Albert A.
Laskaris, Lycurgus
McCarthy, Edith Marie
Plymouth Cordage Company
Post, Frank S.
Roesch, Esther M.
Rupp, Raphael E.
Ryan, George H.
Salter, Wm. Thomas
Spurdle, Robert O.
Stryker, Harvey I.
Vinal, Albert F.
Young, Harry R.
Whipple, Melville C.

NORTH CAROLINA SECTION

Sellers, Walter Bailey

NORTH JERSEY

Bockus, Harry N.
Johnson, Melvin Wesley
Keitel, W.
Murray, Sister Mary Rose
Roberts, Denis

NORTHERN LOUISIANA SECTION

Fulton, Robert C.
McGrath, P. C.

NORTHERN WEST VIRGINIA

Craig, George L.
Donham, Paul J.

OKLAHOMA SECTION

King, Roy E.

PHILADELPHIA SECTION

Bare, Martin K.
Berry, William S.
Braithwaite, Leslie V.
Clemence, LeRoy W.
Endriss, Paul A.
Gruber, Paul L.
Haefelin, H. T.
Ogren, Carl F.
Ozias, Herbert H.

PITTSBURGH SECTION

Crawford, Robert M.
 Dawson, James C.
 Fleming, Harry P.
 Foerster, Charles V., Jr.
 Greek, James A. M.
 Heaston, Elmer J.
 Masters, C. P.
 Munger, Hamnett P.
 Walker, Charles B.

PUGET SOUND SECTION

Bond, Floyd K.
 Church, Anna E.

PURDUE SECTION

Bennett, W. R.
 Curtis, Paul B.
 Evans, Edith N.
 Heck, J. E.
 Matchett, G. R.
 Rothrock, H. S.
 Shock, N. W.
 Swim, F. R.

RHODE ISLAND SECTION

Lyon, Russell D.
 Northup, Harold J.
 Reynolds, Harry H.

ROCHESTER SECTION

Bowman, Clell Edgar
 Phipps, Harris E.

SACRAMENTO SECTION

Richardson, George Arthur

SAINT JOSEPH'S VALLEY SECTION

Flores, Raul

SAINT LOUIS SECTION

Anderson, Wm. B.
 Barr, Frank T.
 Finlay, William James
 Kingsbury, Franklin L.
 Reamon, George W.
 Schilling, Frederick

SOUTH DAKOTA SECTION

Prunty, Earl R.
 Rodman, Ernest A.

SOUTHEAST TEXAS SECTION

Rogers, Walter F.
 Streater, Floyd E.
 Terrell, H. D.

SOUTHERN CALIFORNIA SECTION

Akers, John F.
 Brown, S. M.
 Cumming, Edwin D.
 Jenkins, Grant V.
 May, Bruce M.
 Moon, F. S., Jr.

Voelker, J. F.
 Zabaro, Sidney

SOUTH JERSEY SECTION

Smith, Robert A.

SYRACUSE SECTION

Bingham, Earl P.
 Northrup, Ridgeway

TOLEDO SECTION

Krauss, Carl L.

UNIVERSITY OF ILLINOIS SECTION

Ginnings, D. C.
 King, Edward
 MacQueen, Donald E.
 Partridge, Edward G.
 Pomerene, Elizabeth

UNIVERSITY OF MISSOURI SECTION

Kraft, Ned O.

VERMONT SECTION

Dodge, Ruth A.
 Thomas, Joseph S.

WASHINGTON SECTION

Zornig, Hermann Heinrich

WISCONSIN SECTION

Closs, John O.
 Otterson, Henry
 Ragatz, Roland A.
 Smitz, Louis Z.
 Sullivan, F. T.
 Wiig, Edwin O.

NO SECTION

Acosta, Juan F.
 Allan, William T.
 Allen, Alfred James
 Austin, William Lyle
 Awazu, Saburo
 Bear, Richard S.
 Beatty, Harold A.
 Bennett, O. G.
 Berdoy, Pedro A.
 Birosel, D. M.
 Blume, Paul W.
 Bowers, Rolland G.
 Caselles, Ramon Ramos
 Cheney, Ralph G.
 Clapsadle, Leo
 Cuevas, Sixto
 del Valle, Manuel A.
 Desreets, Luis
 Dewhurst, Milton
 Dixon, L. J.
 Farnell, R. G. W.
 Ferre, Luis Alberto
 Figueroa, Gil
 Fisher, Elmer H.
 Gay, Alfred D.

Gelger, Francis E.
 Good, Adelbert C.
 Guiliassen, J.
 Haeussler, A. F. W.
 Hamilton, P. B.
 Harper, Geo. A.
 Herlin, Clas
 Hickson, Bernard
 Hirako, Doichi
 Hisatake, Isamu
 Hodgkin, Adrian Eliot
 Horsley, Harold
 Hotton, D. H.
 Irizarry, Herminio
 Javierre, Clemente
 Jones, Edward M.
 Korevaar, Ir. A.
 Kuan, Tung-Hua
 Kubokawa, Masao
 Lloyd, John Alexander
 Longinescu, C. G.
 MacLaren, Ian
 Marti, Ramon, Jr.
 Marzzacco, Carl
 Maxim, Mme Marie
 McKay, Donald D.
 Monzon, L. C.
 Mueller, William H.
 Ono, Yuzo
 Osaka, Hajime
 Perez, Arturo Roque

Plambeck, Albert O.
 Ramon, G. A.
 Rivera, Blanca
 Ruigh, William Livingston
 Ruston, Monica Mary
 Sakuma, Noboru
 Saxton, Clement
 Scott, James
 Shaw, Charles New, Jr.
 Shimada, Masayoshi
 Shinagawa, Tadakatsu
 Sigel, Juan
 Silva, Jovito
 Skrimshire, Cecil Geo Hamor
 Skodaworks, Ltd.
 Solomon, Simon
 Stoye, Frank W.
 Swedenborg, Edward A.
 Taketani, Takumi
 Tanaka, Choji
 Tei, John Von Zean
 Tiffeneau, M.
 Vadi, Luis
 Van Melsen, J. A.
 Wada, Isaburo
 Whatmough, W. H.
 Wolochow, David
 Wornum, W. Esmond
 Wylie, Alexander Matthew
 Yamasaki, Yasusuke
 Yorston, F. H.

Proceedings

COUNCIL

President Rosengarten has appointed Professor F. G. Keyes of the Massachusetts Institute of Technology the representative of the American Chemical Society on the Refrigeration Safety Code Committee.

LIST OF MEMBERS ELECTED BETWEEN JANUARY 15 AND FEBRUARY 15, 1927

AKRON SECTION

Hosier, Albert E.
McCutchan, George Lawrence

AMES SECTION

Elmer, Roma C.
McCoy, Orlando Z.
Robinson, J. D.

ARIZONA SECTION

Phelps, Arthur Lee
Welch, Ruth

CALIFORNIA SECTION

Cundall, Roland Lewis
Gale, Laird
Greensfelder, Bernard S.
Higgins, Ralph
Lacomble, A. E.
McCray, Alan A.
Ramsey, William Maxwell
Standard Oil Co. of Calif.

CENTRAL PENNSYLVANIA SECTION

Rumbel, Samuel W.

CENTRAL TEXAS SECTION

de Lorenzi, A. J.
Gibson, James G.
Maisner, Herman
Trow, Richard F.

CHICAGO SECTION

Addleman, Samuel W.
Beeskow, Herbert C.
Blair, Harold T.
Block, Edward
Brooks, Arthur E.
Brunstrum, Lawrence C.
Cohen, Frank
Donham, R. T.
Douthitt, Earl
Ford, Thomas H.
Harr, Russel
Inderdohnen, John F.
Laue, Charles E.
Pearen, C. B.
Price, Harry
Priem, Lillian
Randa, Edward
Scheffler, Edward F.

Scheming, George Michael
Sharp, Agnes
Stanley, Morris R.
Tatar, John E.

CINCINNATI SECTION

Avery, Dustin
Blank, Irvin H.
Crowe, J. B.
Larson, Edwin E.
Sauder, Edward G.

CLEVELAND SECTION

Weygandt, A. S.

COLORADO SECTION

Olcovich, Harold S.
Toyne, Mrs. Emma Johnson

COLUMBUS SECTION

Bloom, Edgar Bennett
Funkhouser, James A.
Ma, Chieh
Wright, Paul M.

CONNECTICUT VALLEY SECTION

Dull, Malcolm F.
Nelson, Paul R.

DELAWARE SECTION

Kenworthy, Edward M.

DETROIT SECTION

Jones, Ralph P.

EASTERN NEW YORK SECTION

Wadsworth, Augustus D.

ERIE SECTION

Anderson, Paul A.

FLORIDA SECTION

Myres, M. J.

FORT WAYNE SECTION

Adams, Paul H.

GEORGIA SECTION

McDaniel, Guy S.
McDonald, Emma
Sutherst, Walter F.

INDIANA SECTION

Cantol Wax Company
Whitacre, Francis M.

IOWA SECTION

Frazer, Glen E.
Jebens, Walter
Wettstein, Thomas F.

KANSAS CITY SECTION

Brodnax, Lewis Meriwether
Brooksbank, J. M.
Lindsly, Charles H.
Morgan, H. T.

LEHIGH VALLEY SECTION

Cantelo, Robert C.
Simmons, C. W.
Thorpe, Melvin A.

LEXINGTON SECTION

Heath, Bennette Legge

LOUISIANA SECTION

Hilman, G. C.
Mexican Petroleum Corp. of La., Inc.
Reid, Alfred Joshua
Wells, Bert H.

MARYLAND SECTION

Herman, Sarah M.
McFerrin, C. Allen, Jr.
Mehring, Arnon L.
Neuman, Emil G.
Williams, James E.

MICHIGAN STATE COLLEGE SECTION

Cole, Ralph Chase
Hardesty, John O.
Kenyon, Marjorie
Maxfield, Frank H.

MILWAUKEE SECTION

Ballard, Grace

MINNESOTA SECTION

Kiess, Matthew
Sorensen, Samuel Olof

NASHVILLE SECTION

Lyon, R. I.
Robinson, Howard W.

NEBRASKA SECTION

Jelinek, Viola C.
Yin-Mei, Lin

NEW HAVEN SECTION

McKesson & Robbins, Inc.
Roberts, Elliott J.
Schairer, J. F.

NEW YORK SECTION

American British Chemical Supplies, Inc.
American Hard Rubber Co.

Batchelder, Esther L.

Byck, Harold T.

Cole, Frank H.

Collin, Philip G.

Ellison, Lee A.

Empire Laboratory Supply Co., Inc.

The Fleischmann Company

The Fleischmann Laboratories

Freeman, John V.

Goldman, Frederick H.

Hartmann, Henry

Honish, John K.

Karolith Corporation

Kastenhuber & Lehrfeld

Lang, Louis

Leonard, Walter B.

Miyamoto, Katsuhel

Ringk, William Frederick

Sobotka, Harry H.

Wong, San W.

NORTH CAROLINA SECTION

Hager, O. B., Jr.

Thomas, Chas. L. M.

NORTHEASTERN SECTION

Callender, R. B.

Chace, William G.

Coughlin, Edward J., Jr.

Daboll, Mary

Engs, William

The Fiberloid Corporation

Hoering, Louise

Gerry, Harold Tirrell

Henderson, Lloyd F.

Lzard, Emmette Farr

Lake, Tyne W.

MacKaracher, D. Fraser

McDaniel, G. Ridgley

Parker, Robert Prescott

Robertson, Donald W.

Schwind, Carl H.

Small, J. K.

Wiley, Ethel

Wilson, Ivan V.

NORTH JERSEY SECTION

Atlantic Coal Tar Distillates

Black, A.

Cooke, H. Harrison

Kahle, Raymond S.

Van Winkle, J. Raymond

NORTHERN WEST VIRGINIA SECTION

Bartlett, J. F.

Brown, C. F.

OKLAHOMA SECTION

Cannon, Lawrence S.

Cunningham, W. K.

Pocock, Luther A.

Watson, M. C.

OREGON SECTION

Carmody, Walter R.

Lothrop, Rex E.

Murray, Hazel C.
Pease, Charles S.
Robinson, Cowin C.
Shea, Thomas F.

PHILADELPHIA SECTION

Boyer, Wm. J.
Claffey, Joseph B.
Greer, Willard N.
Ioannu, John H. P.
Josephita, Sister Mary
Manthroe, Wm. H. J.
McKee, James
Musante, Augustine F. S.
Peet, Charles H.
Troisi, Raphael
Venzke, Herbert F.

PITTSBURGH SECTION

Hoffmann, Alvin A.
Miller, Oscar O.
Murtland, Wm. Owens, Jr.
Sackman, Bruce F.

RHODE ISLAND SECTION

Wooster, Charles Bushnell

ROCHESTER SECTION

FitzSimons, Ogden
Lux, Gerald A.
Molin, Karl Teodor

ST. JOSEPH'S VALLEY SECTION

Toussaint, Walter
Vignos, James C.
Williams, Chas. A.

ST. LOUIS SECTION

Gissel, Elmer A.

SOUTH CAROLINA SECTION

Stephenson, Robert J., Jr.

SOUTHEASTERN TEXAS SECTION

Bernardoni, Bernard
Demmon, R. E.
Garrison, Allen D.
Grant, R. Stephen
Holden, Brian

SOUTHERN CALIFORNIA SECTION

Bilansky, Joe
Brantley, L. Reed
Broun, LeRoy A.
Hanna, J. L.
Harger, Donald K.
Jaxon-Deelman, John
Kerr, W. H.
Kindly, M. M.
Preble, Bennett
Sheffield, Harold C.
Simpson, C. Fillmore
Valvy, Edgar

SYRACUSE SECTION

Fazel, Charles S.
Hepler, Arthur I.
Jones, Russell M.
Rohner, Leonard V.

TOLEDO SECTION

Reeg, Lloyd M.

UNIVERSITY OF ILLINOIS SECTION

Bunney, W. E.
Provine, E. A.
Walsh, Thos. J., Jr.
Ward, Ralph J.
Winters, R. H.
Wolfe, J. E.

UNIVERSITY OF MICHIGAN SECTION

McCabe, Warren L.
Riker, G. E.

VERMONT SECTION

Clark, Ross Lyle
Humphrey, Bingham J.

VIRGINIA SECTION

Bilisoly, J. P.
Hill, H. H.
Johnston, Chas. W.

WASHINGTON SECTION

Clapp, H. G.
Holton, Wm. B.

WESTERN NEW YORK SECTION

Duffield, C. A.
Wetmore, Vera M.

WISCONSIN SECTION

Coon, Ernest D.
Dadswell, Herbert Eric
Fox River Paper Co.
MacKin, John Christopher

NO SECTION

Agathon, Ochine
Ball, Thomas F.
Barnes, William Howard
Roenu, Arthur H.
Bond, Robert W.
Burnell, Dorah L.
Callaghan, E. B.
Chambers, A. R.
Chang, Takufuku
Clarence, Sister M.
Cole, J. E.
Cruz, Hector Edmund
Douglas, G. W.
Douglas, Stuart D.
Finn, Donovan Bartley
Gooddie, John E.
Gratton, George Edward
Hamilton, David J.
Hayashi, Shigeu

Honneyman, William
 Howe, George E.
 Kast, H.
 Kehoe, Julius M.
 Louie, F. S.
 Luciano, Frank
 Langguth, Aloysius B.
 Marples, Alan
 Marvin, R. J.
 Mason, Oliver
 Mizuno, Katsuzo
 Pattee, E. C.
 Petschow, Johannes

Reiber, Harold G.
 Rushton, J. Henry
 Schwartz, Henry P., Jr.
 Senf, Norman Davey
 Travers, Elizabeth
 Traylor, George Hamilton
 Tseng, Chao-Lun
 Twiss, Douglas F.
 The Upjohn Company
 Villalba, Antonio Maria Barriga
 Von Gebauer-Fulwegg, Erich
 Wade, Isaac Worth
 Yamamoto, Iyewo

DECEASED

Chikamori, Seeiichiro, Imperial University, Kyoto, Japan. Died, July 22, 1926.
 Conner, Arthur B., 2123 W. Grand Blvd., Detroit, Mich. Died, January 8, 1927.
 Lyman, James A., 833 Indian Hill Blvd., Claremont, Cal. Died, July 29, 1926.
 Mallick, Paramesh Chandra, 10 Bentinok St., Calcutta, India. Died, July 30, 1926.
 Peters, Hugh H. W., Bureau of Standards, Washington, D. C. Died, January 2, 1927.

Proceedings

COUNCIL

President George D. Rosengarten has appointed Dr. Marston T. Bogert and Dr. Irving Langmuir to represent the American Chemical Society on the occasion of the celebration of the Two Hundredth Anniversary of the Founding of the American Philosophical Society, to be held in Philadelphia, April 27, 28, 29, 30, 1927.

Dr. Lauder W. Jones of Princeton, N. J., and Professor James M. Breckinridge of Nashville, Tenn., have been appointed by President Rosengarten the representatives of the American Chemical Society on the Council of the American Association for the Advancement of Science for 1927.

MEMBERS ELECTED BETWEEN FEBRUARY 15 AND MARCH 15, 1927

AKRON SECTION

Morgan, Paul R.
Royer, George L.

ALABAMA SECTION

Muscle Shoals Fertilizer Co.

CALIFORNIA SECTION

Binkley, Charles H.
Burk, Nowal
Chapman, Lelia Margaret
Foley, J. J.
Hart, Charles Vinton
Krill, Joseph
Philadelphia Quartz Co. of Calif.
Sessions, R. F.
Tomer, Stephen James

CENTRAL PENNSYLVANIA SECTION

American Lime and Stone Co.
Frankenberry, A. W.
Hartswick, Adam Henry

CENTRAL TEXAS SECTION

Millican, Elliott H.
Teal, Gordon K.

CHICAGO SECTION

Anderson, C. H.
Apgar, Frank
Berman, Morris
Chemical Equipment Co.
Clay Products Association
Cook, O. L.
Hyers, William K.
Haroldson, Arthur
Lammers, Franklyn J.
Poindexter, G. G.
Ragins, Ida Kraus
Wing, Wallace E.

CINCINNATI SECTION

Proudfoot, David Gibb

COLORADO SECTION

Collier, Robert Jr.

COLUMBUS SECTION

Bancroft, Richard H.
Deck, Elah M.

CONNECTICUT VALLEY SECTION

Backes, George E.
Henn, Spencer L.

DETROIT SECTION

Jones, Elmer M.

IOWA SECTION

McCormack, J. C.
Skidmore, C. N.

KANSAS CITY SECTION

Clemens, Roe
Ryan, M. M.
Seidlitz Varnish Company

LEHIGH VALLEY SECTION

Baker Chemical Company, J. T.
Butz, Richard J.

LEXINGTON SECTION

Thompson, Charles Middleton, 2nd

LOUISIANA SECTION

Grelis, Edwin J.

LOUISVILLE SECTION

Rethwisch, Francis B.

MARYLAND SECTION

Emerson Drug Company

MIDLAND SECTION

Holmes, Ray D.
Mills, Lindley E.

MILWAUKEE SECTION

Allis-Chalmers Mfg. Co.

MINNESOTA SECTION

Nelson, H. G.
Singley, Charles Earl

NEW HAVEN SECTION

Shepard, Clarence E.

NEW YORK SECTION

Ahrens, Carl
American Schaeffer & Budeberg Corp.
Berkensblit, S. E.
Bright Star Battery Co.
Carnrick, G. W.
Colgate, Robert B.
Consolidated Gas Co. of New York
Coronet Phosphate Company
Drypolcher, W.
Harrison, Lillian E.
Howland, Esther
Nulomoline Company, The
Partridge, Herman M.
Schleifstein, M. L.
Thuesen, Dagfinn
Tirrill Gas Machine Lighting Co.
United States Steel Corp.
Wong, Fred Chew Fui
Zechow, Max Ben

NORTH CAROLINA SECTION

Metsker, John W.

NORTHEASTERN SECTION

Darling, Philip E.
Titherington, Richard H., Jr.
Waite, Alden H.
Waterhouse, H. Y.

NORTH JERSEY SECTION

Bash, Francis F.
Carter, Warren C.
Kirklin, Wayne A.
Sargeant, Stanley M.
Stauder, Edward

NORTHWESTERN UTAH SECTION

Mabbs, John K.

OKLAHOMA SECTION

Beckley, Howard Baxter
Carson, Lamoine S.
Chase, H. D.
Clark, Irwin A.
Mahoney, George F.

OREGON SECTION

Kniaseff, Vasily

PHILADELPHIA SECTION

Etchells, Arthur W.
Godber, Arnold B.
Spreat, Robert
Schoenfeldt, H. Robert

PITTSBURGH SECTION

Murray, Harry Athol, Jr.
Perry, E. R.
Sitzler, Richard R.

PUGET SOUND SECTION

Meyer, H. F.
Wirth, Henry E.

PURDUE SECTION

Hobrock, Raymond H.

RHODE ISLAND SECTION

Pingree, Raymond A.

ROCHESTER SECTION

Rochester Gas & Electric Corp.

ST. JOSEPH'S VALLEY SECTION

Dillon, Henry J.
Slavin, Arthur D.
Wilhelm, Ernest J.

ST. LOUIS SECTION

de Ricci, Sister Catherine
Weirich, Frederick Adam

SOUTH DAKOTA SECTION

Hermanson, Joe L.
Legault, R. R.

SOUTHERN CALIFORNIA SECTION

Fiske, Wilbur A.
Harrower Laboratory, Inc., The
Waynick, D. D.

SOUTH JERSEY SECTION

Davidson, Ruth F.

SYRACUSE SECTION

de Kolumban, Alexander

UNIVERSITY OF MISSOURI SECTION

Schubert, Clarence F.

VIRGINIA SECTION

Harman, Kate E.
Nowlin, G. H., Jr.
Sisson, W. A.
Stone, Edith B.
Zimmermann, Henry D.

WASHINGTON SECTION

May, Orville E.

WISCONSIN SECTION

Popkin, Henry R.

NO SECTION

Burk, C. Franklin
Climax Molybdenum Company
Damard Lacquer Company, Ltd., The
Gloy, Olga Helen Marie
Green, Jesse R.
Hand, Carl N.
Haugan, Harold W.
Harris, Jay Chas.
Herrett, Wilbert A.
Ikushima, Tokio
King, A. T.

Proceedings

GENERAL MEETING MINUTES

The 73rd General Meeting of the American Chemical Society was held at Richmond, Virginia, from Monday, April 11, to Saturday, April 16. The Council meeting was held on the afternoon of the 11th; the general meeting on the morning of Tuesday, April 12; and general divisional meetings of the Biological and Organic Divisions; Industrial and Engineering Chemistry and Sugar Divisions; and the Physical and Inorganic Division, on the afternoon of the 12th. Regular divisional meetings were held all day Wednesday and Thursday. The details of the meeting will be found printed in the News Edition of *Industrial and Engineering Chemistry* for April 20 and May 10.

At the general meeting on Tuesday morning, by recommendation of the Council, the names of Wilhelm Ostwald and Walther Nernst were unanimously restored to the list of honorary members of the American Chemical Society. Also, Richard Willstätter having been duly proposed by ten members of the Society, and having received the endorsement in writing of a majority of the Council, was unanimously elected to honorary membership in the Society.

On Wednesday evening in the auditorium of the Jefferson Hotel an address by Dr. Victor C. Vaughan entitled "A Chemical Concept of the Origin and Development of Life," was delivered by his son, Dr. Warren Vaughan, Dr. Vaughan himself being unavoidably detained by illness. Some 1300 attended the lecture with 300 turned away on account of inability to secure standing room.

The registration showed 1317 members and guests present. The Society was welcomed by Attorney General Saunders on behalf of the State and by Mayor J. Fulmer Bright of the City of Richmond. A response by President Rosengarten followed.

On Monday evening a supper dance was enjoyed by some 400 members and guests.

On Tuesday evening an informal reception crowded the auditorium of the Jefferson Hotel to its limits. The members and guests at this reception were entertained by The Sabbath Glee Club, a colored organization, whose singing of negro spirituals will be long remembered by those who were permitted to be present.

The Garden Party on the afternoon of Wednesday, April 13, at the University of Richmond was especially enjoyed, as it gave the members an opportunity of meeting many Richmond people; of seeing the attractive grounds of the University; and of inspecting the new chemistry building which had been dedicated the previous Monday afternoon.

The dance on Thursday evening interspersed by colonial dances and costumes, by puppets of Miss Eleanor Fry, again crowded the auditorium.

On Friday some 300 attended the barbecue and fish fry at Williamsburg and viewed the interesting historical surroundings of colonial Virginia, with a special trip to Jamestown, some eight miles away. A smaller party, but none the less enjoyable, made a trip to the University of Virginia and Charlottesville and to Jefferson's old home at Monticello on Saturday.

The Agricultural and Food; Biological; Chemical Education; Dye; Gas and Fuel; Industrial and Engineering; Medicinal Products; Paint and Varnish; Petroleum; Physical and Inorganic; Rubber; and the Water, Sewage and Sanitation Chemistry Divisions held divisional meetings. Numerous luncheons and dinners were held by special groups.

Two hundred and ninety-five scientific papers and addresses were offered at the meeting. Possibly the chief feature that impressed all of those in attendance was the warm hospitality from the Virginia city and all its inhabitants in which the meeting was held. Every member attending the meeting felt that he was the personal guest of the Virginia Section.

CHARLES L. PARSONS, *Secretary*

DIRECTORS' MINUTES

The Directors of the American Chemical Society met in the Jefferson Hotel, Richmond, Virginia, Monday, April 11, at 9 P. M., with President Rosengarten in the chair and the following Directors present: W. D. Bancroft, W. D. Bigelow, James F. Norris, S. W. Parr, Charles L. Reese and Charles L. Parsons.

The Treasurer reported the Purchase of \$60,000 par value of Temporary Investments, as follows:

Purchased Jan. 28, 1927:

\$10,000 N. Y. City 3 $\frac{1}{2}$ %—1954—at 90 $\frac{7}{8}$ %
 \$10,000 N. Y. City 4s—1959—at 99 $\frac{1}{8}$ %
 \$10,000 N. Y. City 4 $\frac{1}{2}$ %—1964—at 102 $\frac{7}{8}$ %
 \$10,000 Federal Land Bank 4 $\frac{1}{2}$ %—1937—at 100 $\frac{7}{8}$ %
 \$10,000 Federal Land Bank 4 $\frac{1}{2}$ %—1933—at 101 $\frac{1}{8}$ %
 \$10,000 American Telephone & Telegraph Coll. Trust 4s—1929—at 98 $\frac{1}{4}$ %

Receipts for the Endowment Fund of

\$5000 from the Philadelphia Section
 \$1000 from the Delaware Section
 \$1138.47 from the Committee

making a total of \$36,138.47. This has been invested as of February first in the real estate mortgage we hold, in which the rest of the Fund participates. This investment releases a corresponding amount of funds for the General Fund which will be permanently invested in the near future.

The Treasurer also reported that the income from the Endowment Fund had accumulated to the extent of \$1,674.75 and that a reduction of twenty-five cents per hundred-weight had been made in the price of the paper for the journals of the Society. The report was approved and accepted by the Directors and the Treasurer was instructed to await special appropriations by the Directors at a later date of the income from the Endowment Fund to the journals of the Society.

The Directors voted that the Society should not hold an exposition at the Detroit Meeting of the Society owing to the peculiar conditions there, but that they were quite willing that the Detroit Section should do so if it saw fit and would coöperate with the Society's business manager in the matter of procedure in order that it might be coördinated with Society policy.

The Directors then adjourned.

CHARLES L. PARSONS, *Secretary*

COUNCIL MINUTES

The meeting of the Council of the American Chemical Society was called to order by President Rosengarten at 10.00 A. M., in the Jefferson Hotel, Richmond, Va., on Monday, April 11, with the following Councilors and substitutes present:

Ex-Officio.—W. D. Bancroft, W. D. Bigelow, George C. Brown, Marston T. Bogert, F. B. Carpenter, W. D. Collins, E. J. Crane, M. L. Crossley, Charles H. Herty, B. S. Hopkins, H. E. Howe, E. F. Kohman, John R. Murlin, James F. Norris, W. A. Noyes, S. W. Parr, Charles L. Parsons, H. A. Shonle, Edgar F. Smith.

Councilors-at-Large.—Roger Adams, Edward Bartow, E. M. Billings, A. M. Comey, W. Lee Lewis, S. C. Lind, Harlan S. Miner.

Local Sections.—Akron, A. M. Hamblet. *Central Pennsylvania*, E. D. Ries. *Chicago*, D. K. French, W. S. Hilpert (subs. for W. R. Smith), Walker M. Hinman (subs. for David Klein), Wm. Hoskins, Charles D. Hurd (subs. for Paul Van Cleeft), F. W. Sullivan, Jr. (subs. for H. E. Barnard), E. H. Volwiler, S. C. Langdon (subs. for H. G. Walker). *Cincinnati*, Charles R. Bragdon, C. F. Long (subs. for Martin H. Fischer). *Cleveland*, Hippolyte Gruener, O. F. Tower. *Colorado*, G. H. Whiteford

(subs. for L. D. Roberts). *Columbus*, W. C. Ebaugh, Wm. Lloyd Evans (subs. for Wm. McPherson). *Connecticut Valley*, Joseph S. Chamberlain, Mary L. Sherrill (subs. for C. R. Hoover). *Delaware*, J. L. Bennett, Charles L. Reese. *Detroit*, H. C. Hamilton, Oliver Kamm. *Georgia*, L. B. Lockhart (subs. for T. C. Law). *Illinois-Iowa*, H. A. Geauque (subs. for O. K. Smith). *Indiana*, Edgar B. Carter. *Iowa*, L. Chas. Raiford. *Kansas City*, F. B. Dains, Carl I. Johnson (subs. for H. P. Cady). *Lehigh Valley*, G. A. Menge, Charles C. Nitche. *Lexington*, R. N. Maxson. *Maine*, C. A. Brautlecht. *Maryland*, J. C. W. Frazer, Neil E. Gordon, A. H. Marshall. *Michigan State College*, Arthur J. Clark (subs. for Ward Giltner). *Minnesota*, M. C. Sneed. *Nashville*, J. M. Breckenridge. *New York*, S. P. Burke, C. R. Downs, Thomas B. Freas, Martin H. Ittner, James Kendall, D. H. Killeffer, Sidney D. Kirkpatrick (subs. for Chas. A. Lunn), Herbert R. Moody, Marie Reimer, R. R. Reushaw, Foster Dee Snell, F. W. Willard (subs. for A. W. Thomas), W. W. Winship (subs. for J. G. Davidson), Lois W. Woodford (subs. for B. F. Brooks). *North Carolina*, A. S. Wheeler. *Northeastern*, Winthrop C. Durfee, Gustavus J. Esselen, Jr., Arthur J. Hohman, Arthur D. Holmes, Robert W. Neff, Lyman C. Newell (subs. for W. L. Jennings), John A. Seaverns (subs. for L. A. Pratt), Wilhelm Segerblom. *Northern West Virginia*, C. A. Jacobson. *North Jersey*, Herbert H. Baldwin (subs. for F. W. Zons), Robert P. Fischella (subs. for L. V. Redman), C. O. Johns, David Wesson. *Northwestern Utah*, Frank K. Cameron. *Philadelphia*, C. S. Brinton, J. Bennett Hill, J. Spencer Lucas, Hiram S. Lukens, Horace C. Porter, Wm. Stricker, Walter F. Jaggart. *Pittsburgh*, A. C. Fieldner, J. H. James, Alexander Silverman. *Purdue*, A. R. Middleton. *Rhode Island*, Robert P. Chambers. *Rochester*, W. R. Bloor (subs. for H. Le B. Gray), H. F. Clarke. *Saint Joseph Valley*, J. A. Nieuwand. *Saint Louis*, L. McMaster (subs. for F. R. Ball), Percival Robertson (subs. for E. J. Sheppard), L. A. Watt. *South-eastern Texas*, L. S. Bushnell (subs. for H. B. Weiser). *Southern California*, Walter A. Schmidt. *South Jersey*, R. E. Rose. *Syracuse*, R. A. Baker. *Toledo*, Harold E. Mersereau (subs. for George H. Anderson). *University of Illinois*, D. B. Keyes, A. M. Buswell. *Vermont*, P. Conant Voter (subs. for S. F. Howard). *Virginia*, Edwin Cox (subs. for H. K. McConnell). *Washington*, D. C., V. K. Chestnut, W. Mansfield Clark. *Western New York*, L. F. Hoyt (subs. for J. A. Handy), Walter Wallace (subs. for E. R. Riegel). *Wisconsin*, J. H. Mathews (subs. for Homer Adkins), George J. Ritter (subs. for L. F. Hawley).

A petition in due form was received for the formation of a local section with territory comprising the Island of Porto Rico and with headquarters at Mayaguez, P. R., to be known as the Porto Rico Section. The Council authorized the granting of a charter to the Section.

A petition in due form was received for the formation of a local section to be known as the Ohio Northern Section, with territory comprising the Counties of Hardin, Hancock, Putnam, Allen and Auglaize in the State of Ohio, and with headquarters at Ada, Ohio. The Council authorized that a charter be granted the Section.

A petition was also received in due form for the formation of a section to be known as the Princeton Section, with headquarters at Princeton, N. J., and comprising territory in Mercer County within five miles from Princeton, N. J. The Council authorized that a charter be granted the Section.

The Council voted to authorize the formation of a Paint and Varnish Division of the American Chemical Society, the Paint and Varnish Section having held six successful meetings with a large and enthusiastic attendance and having duly petitioned to be given divisional status. The following by-laws were presented, and having been found to be in conformity with the Constitution and By-Laws of the American Chemical Society were approved by the Council:

BY-LAWS OF THE DIVISION OF PAINT AND VARNISH CHEMISTRY

ARTICLE I—MEMBERSHIP

Membership in the Division, shall be open to all members of the American Chemical Society, and any member of the Society shall, upon request to the Secretary of the Division, be registered as a member of the Division.

ARTICLE II—OFFICERS

Section 1.—The officers of the Division shall be a chairman, a vice-chairman, a recording secretary and an executive committee.

Section 2.—The chairman, vice-chairman and secretary shall be members of the Executive Committee ex-officio.

Section 3.—The Executive Committee shall consist of three registered members of the Division and the members ex-officio, provided by Section 2 of this article. The chairman of the division shall be chairman of the Executive Committee.

Section 4.—At the first session of the Division coincident with the annual meeting of the Society and following the report of the Secretary, the chairman shall appoint from the members present, at the meeting, a committee of three, whose duty it shall be to nominate officers for the ensuing year. This committee shall present the list of nominations immediately preceding the election of officers at the last session during that annual meeting.

Section 5.—All officers of the Division shall be elected annually by ballot at the last session of the Division held during the annual meeting of the Society, and shall take office at the close of the meeting, following the report of the Secretary, the chairman shall appoint from the members present, at the meeting, a committee of three, whose duty it shall be to nominate officers for the ensuing year. This committee shall present the list of nominations immediately preceding the election of officers at the last session during that annual meeting.

Section 6.—The Executive Committee shall fill any vacancies occurring through death or resignation among officers of the Division.

Section 7.—It shall be the duty of the chairman to represent the Division in the Council of the Society, to preside at meetings of the Executive Committee, to carry into effect the decisions and recommendations of that committee, to preside at stated meetings of the Division, and to report to the Society at its regular meetings.

Section 8.—In the absence of the chairman, the duties of the office shall devolve upon the vice-chairman, with one exception, he can attend Council Meetings in the absence of the chairman, but as Councilors have no proxy he has no vote.

Section 9.—It shall be the duty of the recording secretary to keep a record of the proceedings of the Division and of the Executive Committee, to maintain a list of registered members, to send to registered members such notices as the business of the Division may require, and to transmit to the Secretary of the Society the names of all the officers and standing committees of the Division within three weeks of their appointment; and, in like manner, to notify the Secretary of the Society of any change of officers or standing committees during the year.

Section 10.—The recording secretary shall be the custodian of the files of the Division. He shall have charge of the funds of the Division and shall make all disbursements, subject to the authorization of the Executive Committee. He shall report to the Division at its annual meeting.

Section 11.—The Executive Committee shall conduct the business of the Division and direct its activities. The committees shall at each general meeting of the Society, and as early as may be, hold a meeting to consider the affairs of the Division and receive reports of its committees. The voting majority of the Executive Committee shall be responsible for all expenditures which it may authorize, except so far as the action of the council shall previously have provided for such expenditures.

ARTICLE III—MEETINGS

There shall be a meeting of the Division at each general meeting of the Society. Business affecting the organization of the Division shall be transacted only at the meeting coincident with the annual meeting of the Society.

The order of business shall be as follows:

- Reading of minutes.
- Report of executive committee.
- Report of secretary.
- Report of Committees and discussions.
- Reading of papers.
- Miscellaneous Business.

And at the annual meeting:

- Appointment of Nominating Committee.
- Report of Nominating Committee.
- Election of officers.
- Unfinished business.

The regular order of business of the Division may be suspended at any session by the consent of three fourths of the members of the Society present.

ARTICLE IV—SPECIAL COMMITTEES

Section 1.—The Chairman shall with the advice and approval of the Executive Committee, appoint from time to time standing committees of the Division to consider, conduct and report upon such special matters as may be delegated to them. The following committees shall be appointed at the annual meeting or as soon thereafter as may be expedient.

1. Committee on Programs.
2. Committee on Research Problems.
3. Committee on Advertising.

Section 2.—The recording secretary of the Division shall be chairman of the program committee.

ARTICLE V—PAPERS

Section 1.—All titles and outlines of papers must be sent to the recording secretary of the Division at least fifteen days before the program must be sent to the Secretary of the Society.

Section 2.—All papers must be sent to the recording secretary of the Division at least thirty days before the meeting. The exact date will be definitely stated in the preliminary program announcement of each meeting.

Section 3.—Papers shall not be presented on the program at the regular meeting of the Society unless they have been approved by the program committee.

ARTICLE VI—PUBLICATIONS

The official organ of the Division shall be the *Journal of Industrial and Engineering Chemistry*.

The executive committee may at its discretion, provide for the issue of other non serial publications for distribution to registered members of the Division or for sale.

ARTICLE VII—ASSESSMENTS

The Executive Committee may at its discretion impose dues not to exceed three dollars (\$3.00) per year upon registered members of the Division, said dues to be collected by the Secretary and the receipts therefrom to be devoted to the purposes of the Division.

ARTICLE VIII—AMENDMENTS

These by-laws may be amended at any annual meeting of the Division by a three-fifths vote of the registered members present, provided two weeks notice of the proposed amendment with the text thereof has been sent to the registered members of the Division. Amendments to be effective, must be approved by the council and accepted by that body as not inconsistent with the constitution and by-laws of the Society.

It was unanimously voted that the Council recommends to the General Assembly that the names of Walther Nernst and Wilhelm Ostwald be restored to the list of Honorary Members of the American Chemical Society.

Upon recommendation of the Executive Committee, it was voted that rebates paid to local sections on first membership dues secured and forwarded to the Secretary under the regulations established by the Council shall be limited to applicants residing within the territory of the local section which makes claim for rebate.

The following motion was passed at the Philadelphia Meeting:

"A motion that the spring meetings for 1929 and 1930 be omitted was referred to the Executive Committee for consideration and report at the Richmond Meeting."

The Executive Committee reported as follows:

The Executive Committee, after carefully considering the subject of whether the Society shall hold one or two meetings a year, and having read all published arguments presented from the local sections, is unanimously of the opinion that the present plan of at least two meetings a year should be continued as long as the Society has invitations from its local sections and there is the big demand for general meetings of the Society throughout the country that today exists.

They believe that the subject should be considered from the standpoint of service to the science and to the profession rather than from the standpoint of the convenience of individual members. Indeed, they believe that the welfare of the individual member is thus conserved, as two meetings a year bring the meetings twice as often to those chemists who are unable to attend at a distance and the average member's chance of attending is therefore twice as good. They believe it important that as many members as possible come in personal contact with the work of the Society and that the Society's prestige and influence be exerted as often as possible upon the different sections of our country in order that the message of chemistry may be brought not only to the chemist but to the public.

Furthermore, being hosts to the parent society is important to a local section, as it increases local interest and prestige and enables many chemists to attend who would never do so otherwise. They believe that the programs, even with two meetings a year, are well attended and the demand for place has grown. More and more papers, and more and more important papers, are being presented at every meeting, and no meeting of the Society in recent years has failed to have a lasting influence in the development of American chemistry and American chemists. Even with two meetings a year, the programs are already too crowded and the difficulty of finding meeting rooms conveniently located and of sufficient size is great. With one meeting a year, these difficulties would be increased to an extent that they could be handled only in the very largest cities and by our larger sections. Even these larger local sections could scarcely expect a meeting oftener than once in twenty or twenty-five years. To deny the smaller sections the opportunity of a general meeting, or to deny the less populous sections of the country a general meeting from time to time, seems unfair to those sections and those regions. One meeting a year would of necessity lead to this result. Also two meetings are necessary to handle effectively the business of the Society.

The chief plea against two meetings a year appears to be that it is hard for individuals to attend two meetings and to travel the distances required, also that it keeps members from attending the meetings of other chemical organizations. These reasons do not appear valid to the Executive Committee, and they can neither approve handicapping the American Chemical Society in favor of other organizations, nor in keeping the opportunity of attending general meetings from many members of the Society because some find it impossible to attend.

The Council voted unanimously to accept and adopt the report of the Executive Committee.

An invitation from the Columbus Section for the American Chemical Society to meet in Columbus, Ohio, in the spring of 1929 was unanimously accepted.

The Secretary gave notice that he had on record an invitation from the Georgia Section that the Society meet in Atlanta in the spring of 1930 and that invitations had already been announced for the fall meeting of 1929 in Chicago and 1930 in Cincinnati. These invitations were continued on the table pending the time when they might be constitutionally considered.

The Council voted that in view of the special conditions at Detroit it was inexpedient for the Society itself to hold an exposition in Detroit.

S. W. Parr was elected a member of the Executive Committee to fill the unexpired term of George D. Rosengarten. This position was made vacant by his election to the presidency of the Society.

The Executive Committee recommended to the Council that the following report of the Committee on Entrance Requirements presented at the Philadelphia meeting (see *Proceedings, 1926*, p. 47) be adopted.

After extended discussion of the report the Council simply voted that it be accepted with thanks.

The report of the Committee to consider the admission of non-members of the Society to American Chemical Society Meetings, with minor changes in wording suggested by the Membership Committee, was adopted as follows:

Report of Committee to consider the admission of Non-Members to American Chemical Society Meetings.—Your Committee has carefully considered the questions referred to the Divisional Officers Group at the Tulsa Meeting in the spring of 1926, and recommends as follows:

The practice of permitting non-member chemists, resident in the United States, to register at and attend National, Divisional and Regional Meetings, should be continued.

In order to facilitate the classification of registrants at National, Divisional and Regional Meetings, it is recommended that all registrants be required to state on the registration form whether they are members in good standing of the American Chemical Society, and if not, whether they are chemists.

Your Committee recommends that individuals who are American Chemists, but are not members of the Society be required to pay a higher registration fee, and that such persons be provided with distinctive badges, in order to differentiate them from members of the Society and from foreign and non-chemist guests. It is further recommended that the Secretary of the Society be instructed to write to each such registrant a personal letter urging him to join the Society, and enumerating the various reasons for so doing.

Your Committee is of the opinion that admittance to Divisional sessions in National and Regional Meetings be limited to registered individuals.

It is suggested that the Council definitely adopt the policy of not permitting chemists who are resident in the United States but not members of the Society, to present papers at Regional, Divisional or General Meetings of the Society.

Your Committee recommends that the practice of electing associate members to local sections be continued, but that such associate members be denied the privilege of voting and holding office. It is felt that the principle of associate membership could well be employed by officers of local sections for the ultimate induction of new members into the National Society.

H. T. Clarke, *Chairman*, M. T. Bogert, B. S. Hopkins, W. J. Kelly, S. W. Parr, H. B. Weiser, R. E. Wilson.

The following regulations proposed by the committee to consider regulations for the election of honorary members in the Society, and consisting of Marston T. Bogert, *Chairman*, and Messrs. Roger Adams, John Johnston, Arthur D. Little and Julius Stieglitz, were adopted by the Council as procedure to be followed in the proposal and election of honorary members:

(a) Any person whose achievements in Chemistry entitle him to special recognition as an authority in theoretical or applied chemistry, may be nominated for election as an Honorary Member. Such nomination must be presented in writing, signed by at least ten members of the Society, and must set forth in detail the scientific accomplishments upon which the nomination of the candidate is based.

(b) All such nominations shall be filed with the Secretary of the Society, who shall refer them immediately to the Executive Committee.

(c) Upon receipt of every such nomination, the Executive Committee shall designate promptly a special committee (a separate committee for each individual case) of seven members of the Society, five of whom are recognized leaders in that branch of chemistry in which the candidate has achieved his reputation and which is the basis of his nomination, and two others eminent in other branches of chemistry. This special committee shall investigate the merit of the nominee and report its findings to the Executive Committee, who shall in turn transmit it verbatim, together with a report of its own recommendations, to the Council. Unless at least six of the seven members of the special committee approve the nomination, the Executive Committee is instructed to reject it.

(d) Report of the Executive Committee to the Council provided for in (c), after presentation to the Council shall be laid on the table as a special order for the next succeeding meeting of the Council.

(e) Only those individuals whose nominations have been approved by six of the seven members of their special committees can be recommended by the Council for election as Honorary Members, and this recommendation must include the written endorsement of the nominee by at least a majority of the membership of the Council.

(f) Nominations for Honorary Members, recommended by the Council as prescribed above, shall be presented at the General Meeting immediately following the adjournment of that Council meeting at which the nominations were recommended, and shall not be acted upon finally until the next succeeding semi-annual meeting.

(g) Not more than two Honorary Members shall be elected at any one meeting.

(h) The total number of Honorary Members shall not exceed thirty-five.

The report of the Editor of *Scientific Monographs* and the report of the Editor of *Technologic Monographs* were read to the Council, giving a statement of progress in the publication of Monographs and plans for future procedure. These reports were ordered filed.

Other Committees of the American Chemical Society reported as follows:

Committee Advisory to the Bureau of Mines and Bureau of Standards on Non-Ferrous Metals.—William B. Price, the representative of the Society on this Committee, reported the subjects that had been discussed at the Bureau of Standards during the past year. He further reported that no meeting was held at the Bureau of Mines.

Committee Advisory to the War Department.—The Committee Advisory to the War Department has been in conference with the Secretary of War on the matter of the Geneva Protocol, which was referred by him to the Secretary of State, and the result of this conference has been published in the form of letters to and from Secretary Kellogg in the *News Edition* for December 10, 1926 and January 10, 1927.

The Committee has also been in conference with the Quartermaster General with further reference to the dyeing of uniforms, experiments regarding which are still in progress.

Committee on Analysis of Commercial Fats and Oils.—The Committee reported that its report with detailed methods was published in the December, 1926, issue of *Industrial and Engineering Chemistry* and that the Committee was continuing its work.

Committee on Chemical Education.—The Committee of Chemical Education is so closely allied with the Senate of Chemical Education that it is difficult to report upon its work as a separate unit. A special committee of the Senate was appointed at the Philadelphia Meeting of the Society to report any improvements in this alliance. Both the Committee and Senate would appreciate suggestions from the Council.

The organizations are now functioning as follows: The members of the A. C. S. Committee of Chemical Education are ex-officio members of the Senate and the chairman of the said Committee is also chairman of the Senate. After a measure has been passed by a majority of the Senate it is placed before the A. C. S. Committee acting as a separate body. If a majority of the committee pass on it favorably it is taken by the Chairman to the Council for its approval. If it is not passed by a majority of the Committee it goes back to the Senate and if passed by a two-thirds vote is taken directly by the said chairman to the Council.

This type of an organization is to prevent the Council being bothered with trivial matters, and at the same time allow the Senate to make a direct appeal to the Council. It seems logical that the Senate should have a Council hearing on a two-thirds vote since they are a true representative cross-section of the country both geographically and educationally.

The alliance covers all measures whether they originate in the Senate or A. C. S. Committee. This point is well illustrated by the projects which are now before these two bodies. The two principle projects which have been developed during the past year are: (1) A revision of the Correlation of High school and college chemistry; and (2) Research Institute for Chemical Education. The former was started in the committee while the latter originated in the Senate.

Correlation of High School and College Chemistry.—The correlation syllabus has been revised according to the copy attached and has been passed by the Senate and is now before the Committee for their final approval. If you get no further notice before the Council Meeting please accept this report as final and present it to the Council for their approval.

Research Institute of Chemical Education.—The Research Institute of Chemical Education has been approved by the Senate by a letter ballot. It is now before your Committee of Chemical Education. If you get no notice to the contrary before the Council Meeting it will have been approved by the Committee and you are hereby requested to present the project for the approval of the Council.

Find full description of the Institute attached. (For description see *Journal of Chemical Education* for January, 1927.)

The Chairman of the Committee on Chemical Education in presenting the above report offered on behalf of the Senate of Chemical Education the following resolution:

The A. C. S. Committee on Chemical Education, in cooperation with the Senate of Chemical Education, moves that the Council of the American Chemical Society approve the establishment of an Institute for Chemical Education with the understanding that all plans, including the method of the appointment of the Board of Trustees, the ways and means of financing, the type of organization, the location of the Institute and its relation to the cooperating institute or institutions be submitted to the Council by the Senate and Committee of Chemical Education before any definite action is taken.

After discussion, the Council voted to refer this motion to the Executive Committee with the request that they report at the Detroit Meeting of the Council.

Committee on Chemical Engineering Education.—For any intelligent presentation of what educational training is most suitable for the development of a chemical engineer, it would seem wise at the outset to make brief reference to the term "Chemical Engineer." To attempt the formulation of a definition, however, would be simply to thrash over the disputations of the last 10 years and all to little or no purpose, for the simple reason that definitions grow and are not made, and for the further reason that definitions of any sort and in any circumstance are not easily made. It is a question whether they should be attempted at all except as they develop themselves, and grow out of experience. Certainly in any new field they should be left sufficiently flexible to respond to developing conditions. In any event or at any time a definition can only with safety be expressed in very general terms, and the broader the field the more general the definition must be.

For example, an engraver is "One who engraves." (Webster). That definition is safe. It very wisely does not attempt to tell whether such a person works on tombstones or is a Roycroft. Suppose you try to define a lawyer. The moment we attempt anything but a broad and comprehensive statement we will begin to draw boundaries between the fundamentalist who thinks in terms of the underlying principles of justice and equity, and the mere manipulator or operator.

Again it is very difficult to define the term "Engineer." Construction and operation have so largely featured his activities that he has for the most part left the fundamentals behind or transformed them to working formulas. He has in fact left a large part of the field of physics to one side, and all of Chemistry, therefore it is quite evident that a Chemical Engineer who utilizes the whole field of Chemistry and a goodly portion of the field of physics cannot be defined simply as another type of engineer.

However, notwithstanding the difficulties involved in the matter of definition, at the most a subordinate feature, it is not only possible but highly important that the situation be carefully studied and a broad and comprehensive view taken of this new and tremendously important field of activity. It is both appropriate and essential at this evolutionary and indeed revolutionary stage of development, that the American Chemical Society should set forth, so far as possible the fundamental factors which deserve consideration at the present time, in meeting the need of suitably trained men who can function properly under this designation.

We would like to set forth a few observations bearing upon the case as follows:

(1) The American Chemical Society with a membership of approximately 15,000, over 15 per cent. of whom classify themselves as chemical engineers should have a dominating voice in formulating the requirements for the training of a chemical engineer.

(2) The field of constructive development and production now opening along chemical lines is so broad in scope and so great in potential magnitude, and carries with it such vast possibilities for human welfare that it should not be narrowed to any adjunct or appendage of existing groups but be given full freedom of development in its own right and in its own sphere.

(3) It will be unfortunate for all concerned if small or inconsequential differences divide our councils, for chemically speaking there is nothing more clearly evident than that in the future as in the past, "In union there is strength."

(4) It is doubtful if at any time hard and fast rules for the training of Chemical Engineers may wisely be formulated. At least in the present stages of development a flexibility should be maintained that shall meet the wide variation both in the requirements of the field and in the educational facilities for meeting them.

(5) It seems to be the opinion of not only educators but industrial executives that a chemical engineer should have a thorough and extensive training in chemistry, physics and mathematics. Very little time should be spent in any specialized subject. Practice schools including the testing of large scale equipment of all types are fast becoming popular as did the large scale process laboratory of a few years ago. The committee recognizes the value of these new types of instruction but as stated above the extreme importance of teaching the very fundamental sciences should be persistently observed.

(6) This committee is not in favor of setting up an approved list of chemical engineering schools. Such a list is bound to result in discord, personal animosities and worst of all have a tendency to stifle individual initiative and standardize the teaching of chemical engineering throughout the country. This standardization of education has already produced disastrous results in this country and every effort to prevent its spreading further should be made.

(7) For the benefit of those small institutions which are not familiar with the growth and progress of chemical engineering it would be wise to suggest various worth-while curricula and also to make additional suggestions from time to time.

(8) In order to prevent duplication of effort which would be extremely serious in this particular case, the committee would recommend that they confer with the committee on Chemical Engineering Education of the American Institute of Chemical Engineers to the end that they may utilize the very excellent review and results of many years of work by the American Institute Committee and incorporate as much as possible in a report for the American Chemical Society. Furthermore, that this report on Chemical Engineering Education should be published by the American Chemical Society and distributed to all its members. This is of course with the assumption that the report will be accepted by the American Chemical Society.

Committee on Cooperation with the Chemical Warfare Service.—The Committee held its last general meeting in June 1926, since which time the procedure recommended by the committee has been followed. This has involved meetings of the several subcommittees at the Arsenal, each group concentrating for two or more days upon the phases of the work with which it is most familiar and at the same time obtaining a general impression of research in progress and of conditions in general. In addition, individuals have been called upon by the Arsenal for advice and suggestions and members of the scientific staff of the Arsenal have also been sent out to call upon consultants and other specialists in their own laboratories and plants. Arrangements are now being made for an early meeting of the entire committee at the Arsenal.

Corrosion Committee.—The Committee reported progress.

Endowment Committee.—The Committee reported that the Endowment Fund had been increased by something over \$7,000 during the past year. The Committee has held meetings, discussed procedure, and has been making plans towards the further development of its campaign.

Exchange Committee.—The Committee reported 41 new exchanges made in the past year, the list being submitted to the Council for filing.

Finance Committee.—Your Finance Committee has to report that the year 1926 showed satisfactory operation from the money point of view. The receipts were somewhat larger than was anticipated when the budget for the year was drawn, and the expense was slightly less than the budget allowances. This excellent situation changed a slight deficit which appeared in the budget as drawn into a small surplus when the year of operation was ended.

The income and expenses of the Society now are each about \$1000 per day for the 365 days of the year. This is exclusive of various Trust Funds, such as the Decennial Index Fund, Endowment Fund, Morris Loeb Museum Fund, etc. The situation means that the Society is running at almost an even balance of income and expenditures. Daily income has just about doubled since the present Treasurer took office, and expenses have advanced at about the same rate.

The various Trust Funds of the Society are now in the following condition:

Decennial Index Fund unexpended	\$63,709.40
Endowment Fund	36,138.47
Morris Loeb Museum Fund	25,992.25
Life Membership Fund	6,235.04
Priestley Memorial Fund	1,115.75

Guaranteed Reagents Committee.—During the year 1926-7 the committee has continued the preparation of specifications for reagents to be used in careful analytical work. The specifications prepared during the year will be submitted for publication in *Industrial and Engineering Chemistry*.

It is recommended that the name of this committee be changed to Committee on Analytical Reagents, which will indicate better the present work of the committee.

Committee on Hazardous Chemicals and Explosives.—The Committee reported that it has continued its services as a consultant for the Committee on Hazardous Chemicals and Explosives of the National Fire Protective Association and submitted attached to its report a copy of the annual report rendered by the Chairman of that Committee, which was a tentative report and is still under consideration.

Industrial Alcohol Committee.—The Committee reported through its Chairman, Martin H. Ittner. Their report will be found printed in full in the April 20th issue of the *News Edition*.

Committee on Institute for Chemo-Medical Research.—The report of the Committee presented by Chairman, Charles H. Herty, is as follows:

The Committee on an Institute for Chemo-Medical Research begs to report that the outstanding development during the past year was the introduction of a bill in the U. S. Senate by Senator Ransdell of Louisiana which aims to carry out the principles of the Committee's original report through the creation by Congress of a National Institute of Health within the Public Health Service through the expansion of the Hygienic Laboratory.

In a speech on the floor of the Senate at the time of the introduction of a bill Senator Ransdell expressed his indebtedness to our original report for his inspiration in this matter and quoted at length from the report. A reprint of Senator Ransdell's bill and speech is attached to this report as exhibit A.

Following conferences between Senator Ransdell, Surgeon General Cumming of the U. S. Public

Health Service and the Chairman of this committee, Senator Ransdell decided to introduce a new bill combining his original bill with the so-called Parker bill H.R. 10125, a purely administrative measure. This combined bill exhibit B S. 5835 was introduced in the Senate by Senator Ransdell on March 2, 1927.

It is the purpose of the Committee to give Senator Ransdell all possible help in the work of public and official education which must be carried out as an essential factor in the success of this legislation.

The Chairman offered the following resolution, which was unanimously passed:

"WHEREAS the prevalence of sickness among our people, with attendant suffering and economic losses, points clearly to the need of a greater amount of fundamental research and for the alleviation of this condition, and

"WHEREAS all are subject to sickness, all should participate in providing for this necessary fundamental research, therefore be it

"Resolved that the Council of the American Chemical Society approves the principles embodied in the bill S. 5835, introduced in the 69th Congress by Senator Ransdell, providing for a National Institute of Health and for needed administrative reforms in the United States Public Health Service, and urges its early and favorable consideration by the 70th Congress."

Membership Committee.—The Committee reported as follows.

Individual Members elected 1926.....	1,898
Corporation Members elected 1926.....	64
Members Resigned 1926.....	551
Deceased Members 1926.....	66
Total Membership at end of year 1926.....	14,704
Members dropped for delinquency on January 1, 1927.....	66 ⁶

Metric System Committee.—During the year the Metric Committee has devoted its main activity to educating our people to the purchase of chemicals in Standard Metric Packages. Between 25 and 50 thousand Chemrules have been now distributed, and one has been placed in the hands of every chemistry teacher in California, Illinois, Maryland, Virginia, District of Columbia, New York, Pennsylvania and the New England States. Several apparatus firms list the Chemrule in their catalogs and report a ready demand for it. It has been received with favor. A few papers have been presented on various phases of the advance of Metric Measures and the attempt has been made to secure a sum of money for the further prosecution of this work. An article in the *Journal of Chemical Education* has been arranged for.

Committee on Nomenclature, Spelling and Pronunciation.—During the past year your Committee on Nomenclature, Spelling and Pronunciation has continued to receive many requests for information on subjects relating to its field of activity and has endeavored in each case to help. In editing *Chemical Abstracts*, particularly in the indexing, it is necessary for this office to try to keep informed as to best usage in chemical names and spellings. It is not a heavy additional task, therefore, to maintain a kind of clearing house for this kind of information. Individual members of your committee, particularly Dr. Austin M. Patterson, frequently help.

Last fall the report of the Committee on the Nomenclature of Pectin, of the Agriculture Food Division, was referred to your general committee on nomenclature. After a study of this report by each of the sixteen members of your committee certain recommendations were made to the pectin committee which led to the attached revised report. The definitions relating to pectin now have the approval of the general committee and it is recommended that they be adopted as tentative for one year after publication. The pectin committee has done a very thorough piece of work and it has been a pleasure to cooperate with it.

The report referred to above is recorded here as a means of international reference.

DEFINITIONS WRITTEN BY THE COMMITTEE ON NOMENCLATURE OF PECTIN OF THE AGRICULTURE-FOOD DIVISION

Pectic Substances.—A group designation for those complex carbohydrate derivatives which occur in plants, or are prepared from plants and which are characterized by the presence of galacturonic acid units. In the naturally occurring pectic substances, the galacturonic acid units apparently exist in an acid reacting complex associated with arabinose and galactose units. This acid complex may occur as a free acid or as a metallic salt, but usually occurs as a methyl ester.

Protopectin.—The term applied to the water insoluble, unhydrolyzed pectin substances in the state in which they occur in plant tissues. *Protopectins* are rendered soluble by treatment with enzymes, acids or certain other reagents, whether by peptization or hydrolysis not being known. The substances thus rendered soluble are designated collectively as *pectin*; it is not known whether or not the *pectins* are different chemical individuals from *protopectins*.

Pectin.—The term applied to the water-soluble, methylated pectin substances occurring in plant tissues or to the methylated pectic substances obtained by restricted treatment of *protopectin* with *protopectinase*, acids or other reagents, the treatment being so regulated as to produce maximum solution of pectic substances with a minimum cleavage of methyl ester groups. The product may be a mixture of substances of varying methyl ester content; the term *pectin* or *pectins* is accordingly a group designation for all intermediate pectic substances between *protopectin* and *pectic acid*. It is proper, however, to refer to an individual of the group as a *pectin*.

Pectic Acid.—The term applied to the pectic substances obtained by the hydrolysis of *pectin* with the complete elimination of the methyl ester groups. Pectic acid may be variable in composition according to the type of hydrolysis employed; accordingly there may be a number of *pectic acids*, all of which are ester-free.

Protopectinase.—The term applied to the enzyme which hydrolyzes or dissolves *protopectin* with the resultant separation of the plant cells from each other, usually spoken of as maceration. Presumably the product of this hydrolysis is pectin. The term *protopectinase* supercedes the older term "pectosinase" with which it is synonymous.

Pectase.—The term applied to the enzyme which converts *pectin* into *pectic acid*, the latter becoming a gel, especially in the presence of calcium (or barium or strontium) salts.

Pectinase.—The term applied to the enzyme which hydrolyzes *pectin* and *pectic acid* into their simplest soluble cleavage products, which are probably arabinose, galactose and galacturonic acid.

STATEMENT TO ACCOMPANY REPORT OF THE COMMITTEE ON PECTIN NOMENCLATURE

The nomenclature for the pectic substances was arrived at after considerable discussion and correspondence. Since similar discussions are likely to arise again, it appears desirable that a statement be made of the reasons which guided the committee in the wording of each of the definitions.

Pectic Substances.—This name has been used in recent literature by von Fellenberg, Sucharipa, and others, and appears to be almost satisfactory general designation. It appears undesirable that the term *pectin* should be retained as a loose general designation for all substances of this type; this term should rather be restricted to the soluble substances defined under *pectin*, thus obviating the need of the expedient so frequently used in the past, of referring to *soluble pectin* in order to distinguish *pectin* from *protopectin*.

The substances are designated as "carbohydrate derivatives" in contradistinction from "carbohydrates." Pectic substances are distinguished from polysaccharides in general by the presence of carboxyl groups. These carboxyl groups are now known to reside in sugar acid units which presumably originate by the oxidation of alcoholic groups of sugar units. Accordingly it appears consistent with the physiological origin of pectic substances, as well as with their chemistry, to designate them as carbohydrate derivatives.

As far as is known, galacturonic acid units are the only acid units found in pectic substances. It is true that further studies may disclose the presence of other acids and it may prove necessary at a later date to make the definition more general by substituting "hexuronic acid" for "galacturonic acid." Such a generalization appears undesirable in view of the limits of our present knowledge.

The present definition of the pectic substances is intended to confine the term to the gelatinizable substances of the types that are found in fruits, in the succulent edible vegetables, and in cell wall tissues generally. It is intended to exclude plant mucilages, algin-like substances from marine algae, cactus siliques, etc., although these bodies are apparently closely related, chemically, to the pectic substances. From the meager data available, it appears that these substances contain other acid groups than galacturonic acid; for example, Sven Oden reports that presence of a pentonic acid in a preparation from marine algae, and Spoehr asserts that glucuronic acid occurs in cactus. The definition of pectic substances as substances containing galacturonic acid appears to effect the desired distinction from these other classes of bodies.

As far as the committee is aware, all naturally occurring pectic substances contain arabinose and galactose units but in the case of laboratory preparations, the carbohydrate units of the original pectic substance may be partly or wholly split off by the hydrolytic treatment employed. The definition of pectic substances has been worded so as to recognize these facts.

Protopectin.—The original pectic substance has been variously designated as *pectose*, as *protopectin*, and as *pectinogen*. Pectose was named by Frey in 1840, protopectin by Tschirch in 1908, and pectinogen by Schryver and Haynes in 1914. The name pectose accordingly takes priority and is strongly established in the literature of plant physiology. Chemically it is an unfortunate term since the suffix *ose* is almost exclusively reserved for the crystalline sugars (with one important exception—cellulose—which is apparently too firmly established to be changed). Since *protopectin* was proposed by Tschirch in 1908, it has been accepted and used by von Fellenberg, Neuberg, Ehrlich, Sucharipa, and in fact, by practically all pectin chemists of continental Europe. A canvas of American pectin chemists indicates that nearly all of them prefer this term. Some English investigators, on the other hand, prefer and use *pectinogen*, and one American worker has expressed a preference for this term on etymological grounds. Although the derivation would suggest that it refers to the original pectic substance, and although it has been so used, the term pectinogen was created to apply to a soluble pectin isolated by a definite type of treatment. In view of the fact that this term has been used in a dual sense whereby confusion has arisen, and of the fact that the term protopectin takes priority and is already better established, the selection of protopectin as the designation for the original pectic substance appears logical and satisfactory. The term pectinogen is legitimately applied to a soluble pectin prepared by the treatment described by Schryver and Haynes.

Pure protopectin has never been isolated for the reason that it has no known solvents and therefore cannot yet be separated from the accompanying and likewise insoluble cell-wall tissue. Nevertheless, the existence of this substance has been assumed ever since pectic substances were known. From the results of investigations on apple pomace and unripe apples, which appeared to indicate that all of the pectic substances in these materials are water-soluble, Tutin concluded that protopectin has no real existence. It is to be noted that Tutin's investigations were confined to a single type of material, and that, even as applied to this material, his conclusions have been questioned by Carre. Sucharipa, on the other hand, has brought forward direct evidence which apparently indicates that the insoluble protopectin is a pectic substance in combination with cellulose, and that the soluble form is obtainable only after separation from the cellulose by hydrolytic treatment. The committee's conception of the nature of protopectin rests to a large extent upon the evidence submitted by Sucharipa, which in our opinion, is sufficient to justify the recognition of protopectin as a distinct class of pectic substances.

A different view has been recently advanced concerning the nature of the original pectic substance found in the cell walls of plants. According to this view the substance which has been designated as protopectin, is regarded as essentially the same substance as pectin. The proponents of this view reject the conception that the conversion of insoluble pectic substance to pectin under the action of acids or other reagents is necessarily a process of hydrolysis; it is argued that possibly the original undissolved pectin is so strongly adsorbed by the cell-walls, that it cannot be extracted with water whereas it can be extracted by acid. On the basis of this viewpoint, it is contended that evidence is lacking for the existence of protopectin as a separate substance differing from pectin.

It is the opinion of the committee on Pectin Nomenclature that the traditional view, *i. e.*, that the conversion of the original undissolved pectic substance into dissolved pectin is a process of hydrolysis, is the simplest explanation of the observed facts; furthermore, that there is a considerable amount of experimental evidence in support of this traditional view. Strong support for this view is found in Sucharipa's observation that, during treatments which convert the undissolved pectin of plants into soluble forms, a quantity of cellulose is simultaneously rendered soluble in ammoniacal copper oxide solution, and this in regular proportion to the quantity of pectin dissolved. The behavior of plant tissues containing insoluble pectic substances when subjected to the action of enzymes, is especially consistent with the traditional view. On the other hand, it must be admitted that the conception of protopectin as a colloidally adsorbed pectin may be the correct one. However, until evidence is forthcoming which will definitely indicate that protopectin has no real existence as a substance distinct from pectin, investigators will continue to require some term to describe the undissolved pectic substance of the cell wall of plants. Accordingly, it appears to the committee that the definition of protopectin as a separate substance should be retained, but expressed in such terms as will indicate that possibly it may be chemically the same as the soluble pectine.

Pectin.—The definition here given is in conformity with the traditional use of the term in its more restricted sense. There has been some questions as to the advisability of including in this class those members of the pectin family that are free in nature, especially since they tend to show acid characteristics. There are two objections to such a classification: (1) the classification, to be scientific, should be based upon chemical composition or some other accurately ascertainable characteristic, rather than upon commercial value, and (2) it would be very difficult to determine where to draw the line between pectin and pectic acid. Accordingly, the chemical classification has been retained and the presence of methyl ester content is assumed to characterize pectins and to distinguish them from pectic acids which are consequently assumed to be free from methyl ester. (This classification has been used by Sucharipa in his recent monograph, "Die Pektinstoffe," Serger & Hempel, Braunschweig, Germany. See p. 95.)

In stating the type of hydrolysis that produced pectin from protopectin, it is not the intention of the committee to define pectin as the product of a treatment. The defining characteristics of pectins are their methylated condition and (with the possible exception of some slightly methylated pectins), their water-solubility; the phrase "restricted hydrolysis" is introduced to distinguish the preparative treatment of pectins from treatments that would result in pectic acids.

Sucharipa classifies the pectins into (1) *free pectin*, occurring as such in the plant and removable by simple water solution, and (2) *hydrolysis pectin*, resulting from protopectin by treatment with hydrolyzing agents. Chemically, they are distinguished by the fact that the free pectin retains arabinose units while the hydrolysis pectins do not, the pentose units having split off during the hydrolysis. (See citation above.)

The classification offered by the committee affords opportunity for later subdividing the pectins as proposed by Sucharipa, or in other ways. The committee does not consider it advisable to recommend any subdivision of these main groups at present. The committee regards its present task to be the clarification of the general terms used with references to the pectic substances and the grouping of the various recognized pectic substances into their general classes on the basis of their chemical similarity. Once this is accomplished, it will be comparatively easy to decide upon the further subdivision of the groups and to fit individual substances into the general scheme.

Pectic Acid.—Doubt has been expressed as to whether all substances heretofore classified as pectic acids are completely free from methyl ester. If the classification is to have a sound chemical foundation, it appears necessary to assume that we have a sharp separation into *pectins* which are esters and completely de-esterified *pectic acids*. The reasons have already been discussed under the section entitled *pectin*. Further researches may, of course, necessitate reclassification of some of the substances now known as pectic acids, since, if it is found that they still retain methyl ester groups, they will then be regarded under the definition as acid esters, or *pectins*.

The methyl-ester-free pectic acids are probably variable in composition according to the amount and kind of non-methoxyl groups (i. e., arabinose, galactose, etc.) that are retained with them. According to the type of hydrolysis by which they are formed, we may expect to find the groups of the original pectin split off or retained in varying proportion. The pectic acid contained in the calcium pectate of Carre and Haynes, the cytopectic acid of Clayton, Norris and Schryver, and the pectic acid of Wichmann and Chernoff are all regarded as pectic acids under the definition given, but they probably differ in composition as they differ in preparative treatment.

Protopectinase.—In order to conform to the term protopectin, it appears desirable to discontinue the traditional name *pectosinase* for the enzyme which acts upon it, and to substitute the new term *protopectinase*. Although the older term is well established in the literature, it is believed that the introduction of a new term will not cause confusion as the naming of enzyme and substrate follows the usual convention and the significance of the term is self-evident.

Pectase.—In this definition is retained the significance that has been attached to the term ever since it was first stated by Frey. Mention of gel formation gives expression to the recognized coagulating effect of the enzyme.

Pectinase.—This definition also is the traditional one given by Frey. It appears to the committee desirable that these definitions be restated at this time in essentially their original forms.

It has been suggested to the committee that recommendations be made that the terms *metapectin* and *parapectin* be dropped. The committee is of the opinion that these terms are already obsolete and that no useful purpose will be served by making any formal statement concerning them.

Committee on the Nomenclature of Pectin.—C. S. Brinton, U. S. D. A. Food and Drug Inspection Laboratory, Philadelphia.; H. J. Wichmann, U. S. D. A. Food and Drug Inspection Laboratory, San Francisco, Calif.; J. J. Willaman, Division of Agric. Biochem., University of Minnesota, St. Paul, Minn.; C. P. Wilson, Research Lab., Calif. Fruit Growers Exch., San Dimas, Calif.; W. H. Dore (Chairman), Div. Plant Nutrition, Agric. Expt. Sta., Univ. Calif., Berkeley, Calif.

Committee on Occupational Diseases in Chemical Trades.—The Committee reported certain recommendations for the reorganization and procedure of the Committee, which were referred to the President for such action as he deemed wise upon consultation with the Executive Committee.

Paper Committee.—The Committee on Paper for the publications of the American Chemical Society respectfully reports that each of the papers used for the Society's publication is equal in all respects to that used for the past several years.

Patent and Related Legislation Committee.—The Committee made no report.

Committee on Preparation and Publication of a List of Ring Systems Used in Organic Chemistry. (Joint with the National Research Council.)—Publication of the List of Ring Systems still waits on the final adoption of the "Proposed International Rules for Numbering Organic Ring Systems" (see *J. Am. Chem. Soc.*, 47, 543-61 (1925)). The "period of criticism" expired in February 1927 but there may be delay in adoption due to the facts that the Germans have not had an opportunity to vote on the matter and that some chemists favor making exceptions of certain well known systems such as anthracene and purine. Through cooperation with the *Chemical Abstracts* office the manuscript list has been kept up to date; some work remains to be done on the literature of the period 1899-1907 and on the new Beilstein.

Prize Essays Committee.—The fourth Prize Essay Contest for accredited secondary school students was formally launched on October 6, 1926, when letters with booklets and display posters were distributed to 14,423 public and private high schools, all of which schools had previously been sent a gift set of the reference books. The Society has little appreciation of the enormous amount of work necessary carefully to revise and check our school lists. This process during the past year has resulted in the addition of 3503 new secondary schools, to the principal of each of which a special letter was sent with a booklet announcing the fourth contest and offering to supply the set of reference books without charge if the school were interested.

New state committee chairmen were secured in several states this year, some of the former chairmen having asked to be relieved, and other changes being made at the instance of our committee. Some of the state chairmen enter into the work of the contest with enthusiasm, writing personal letters to the high school chemistry teachers, speaking at state teachers' meetings, broadcasting explanations of the contest, and discussing the topics in a series of radio talks, as well as addressing high school student bodies in their own localities. In the states of Pennsylvania and Washington college professors were placed at the call of any high school wishing to be addressed on topics in chemistry and prepared to pay railroad expenses. Many state superintendents of education have officially sanctioned the project and have urged participation in the contest in their bulletin to high schools. In some states our chairmen are inactive with the exception of examining the essays at the close of the contest.

A direct reflection of the good results achieved through the distribution and sale of books by the Chemical Foundation is to be found in the increased number of essays submitted this year on the topic "The Relation of Chemistry to Industry." Approximately 50 per cent. of the purchasers of "Chemistry in Industry" have been high schools and high school students. To date Volume I is in its 55th thousand, Volume II in its 45th thousand, "Chemistry in Agriculture" in its 30th thousand, and 125,000 sets of the five reference books have been sold or given away. Certain individual books in the sets have reached a still higher figure.

Our state chairmen this year comment on the improved quality of the essays and it is apparent that school authorities are devoting more attention to selecting and submitting only their representative essays. For example, one school in Pennsylvania prepared 240 essays, but submitted only 6. It is therefore impossible to estimate exactly how many high school students have participated in this year's contest. But the growth of interest from year to year is apparent and the results appear to justify the expenditure of time, money, and effort involved in the contest.

A partial return indicates that approximately six thousand essays have been actually submitted to state and territorial committees this year, and our records show that approximately 12 per cent. of the secondary schools to which books have been distributed have participated in this year's contest. States having a smaller number of high schools participate per school in much greater proportion than states having several hundred high schools. For instance, New Mexico with 51 secondary schools this year submitted 49 essays, whereas Iowa with 865 schools submitted only 127 essays.

CONTEST FOR UNIVERSITY AND COLLEGE FRESHMEN

It will be recalled that this year the first contest limited to freshmen in our colleges and universities was held as a part of the Prize Essay Contest. Heretofore all classes have been eligible, but the results this year indicate that the new policy is a wise one. In the 1925-26 contest when all classes were eligible to participate, only 360 essays were submitted for the entire country. This year from the freshmen alone 477 essays have been received. These are fairly well apportioned among the six topics.

Our lists show 871 colleges and universities eligible to participate but of these 736 were not represented in this year's contest. Fifteen per cent. or 135 colleges and universities were represented in this year's contest, but it is difficult to approximate the actual number of participants. For instance, 228 essays were prepared at Syracuse University, but only 38 were submitted. North Dakota Agricultural College prepared 200 and submitted 32. Pennsylvania State College wrote 300 and submitted 40, and at the University of Maryland 350 were written and but 31 submitted.

NORMAL SCHOOLS AND TEACHERS' COLLEGE COMPETITION

Two hundred and fifty-eight normal school and teachers' colleges received individual invitations to participate in this new contest, each invitation being accompanied by booklets, display posters and a gift set of the five reference books. Essays from fifty of these schools to the number of 133 have been received from these teacher-training institutions. The committee considers this showing most representative and is confident that a majority of the 208 schools which did not participate this year can readily be persuaded to participate in future contests.

After four years' experience with the various contests sponsored by the American Chemical Society and made possible through the generosity of Mr. and Mrs. Francis P. Garvan, your committee is unanimous in its belief that if the contest is not as successful as it should be, two principal causes are responsible. First, many sections of the American Chemical Society remain inactive so far as the contest is concerned and but a small minority of the local sections consider the contest any of their affair. It is perfectly obvious that the large amount of work incident to the contest could not be carried out but for the very generous support given the committee by numerous individuals and several local sections. The facts remain, however, that the majority of our members seem to feel that after having accepted responsibility for the contest and approving the appointment of a committee, their duty has been performed and they are quite content to let the committee and any others who will perform the work, so long as their own effort is not involved. It ought to be possible to have chemists generally appreciate that one of the results of this contest is the education of the very men by whom they are employed and that they have a direct interest in the education of these executives. More than 40 per cent. of the reference books offered at nominal cost in connection with the Prize Essay Contest have been purchased by executives, financiers and other business men. But this has not been due—with a few notable exceptions—to the efforts of the chemists themselves.

The second difficulty is in the lack of interest on the part of teachers, whether they be in high schools, teachers' colleges, or universities. In some instances the teachers of science together with the teachers of English have realized the potentialities of the Prize Essay Contest as an aid to their own work and the results have been very gratifying, both to the committee and to the teachers themselves, not to mention the measurable benefit to the students. If, for example, teachers in schools generally would show the same enthusiasm for the possibilities of the contest as we have found in Honolulu, all concerned—chemists, teachers and students—would soon come to realize that in this contest we have one of the best opportunities possible for carefully laying the foundation upon which the future progress of American chemistry may very largely rest.

The committee is very glad to be able to transmit to the president and council of the Society the offer of Mr. and Mrs. Francis P. Garvan to sponsor a Prize Essay Contest for the academic year 1927-28 along substantially the same lines as the previous contests, the principal change being in the contest for the college and university freshmen. This coming year will see in place of the one cash prize for the best essay in each of the six groups, three prizes as follows: first, five hundred dollars; second, three hundred dollars; and third, two hundred dollars. This places the prizes for this contest on the same basis as prevail this year for the normal schools and teachers' colleges and the committee believes this will contribute directly to a greater interest on the part of students.

The committee wishes again to thank sincerely the national chairman and the national committee members, the state chairmen and the state committee members, as well as the large group of

individual chemists who have rendered indispensable aid in furthering the work in which we are so deeply interested.

The Council unanimously instructed the Secretary to write to Mr. and Mrs. Francis P. Garvan and express the appreciation of the Society for their continued support of this important work.

Committee on the Revision of Methods of Coal Sampling and Analysis. (Joint with the Society for Testing Materials.)—The Committee reported that their procedure regarding the methods for determining the fusibility of coal-ash had been accepted by the Supervisory Committee on Standard Methods of Analysis and considered their work completed.

Committee on Standard Apparatus.—During the year 1926-7 the committee has made recommendations on a few questions of sizes and shapes of apparatus. Through the coöperation of members of the Association of Scientific Apparatus Makers of the United States of America it has been possible to issue an illustrated report which gives the recommended standard sizes and shapes adopted by the committee. Most of the material was published, without illustrations, in *Industrial and Engineering Chemistry*, vol. 13, page 1070, 1921, and vol. 14, pages 654 and 738, 1922. With the publication of the comprehensive report it will be possible for the committee to survey the field, take up items that have not been considered, and recommend standard dimensions for items that are now listed as "large" or "small," or without any indication of dimensions.

Committee on Standard Methods for the Examination of Water and Sewage to Coöperate with the Committee of the American Public Health Association.—No actual revision work of Standard Methods for the Examination of Water and Sewage is now in progress. A revision according to the usual procedure will be made in 1928. Looking forward to such revision this committee has collected data on the strength of soap solutions used in rating Zeolite water softeners and data on the significance of the albuminoid ammonia test.

The data on soap solutions were presented before the Water Sewage and Sanitation section at the Philadelphia meeting and a resolution was adopted favoring an establishment of a standard soap for this purpose.

Committee on Standardization of Biological Stains.—The representative of the American Chemical Society on this Committee reported as follows:

The Commission on the Standardization of Biological Stains has had a very prosperous year. Further progress has been made along the lines of work previously undertaken. The Standardization of the stains themselves has progressed to the point where thirty seven (37) of the most widely used stains are being certified, against twenty-eight (28) a year ago. The work necessary to the establishment of standards for the stains has led to the development of considerable new information in regard to the dyes themselves and their reactions and properties, from both a chemical and a biological viewpoint. As an example of this, the discovery of the double compounds of basic dyes with phenols may be noted. Formerly it was supposed that the phenol served as a mordant pure and simple. But it has been shown that this idea is false. What really takes place is a combination of the dye with the phenol, forming a new compound with staining properties differing widely from those of the original dye. (*Vide Stain Technology*, 1, pp. 77, 98, 116 (1926).)

The new journal, *Stain Technology*, published by the Commission, made its appearance last January and regularly each quarter since. In the first volume are about thirty (30) articles and notes dealing with new methods or investigations of older methods. More than fifty per cent. of these have been voluntary, unsolicited contributions and the results of work independent of that carried on by the Commission itself. The Journal has been well received and promises to have a successful future.

The Biologists are now more than ever firmly convinced of the value of the closest coöperation between themselves and chemists. And the work of the Commission has shown that the chemist can learn much by working alongside the biologist. Both types of scientific work have been benefited largely by this association and the future is bright with the promise of further important developments of interest to both sciences. It is therefore recommended that this Society continue its representation on the Commission by appointing a successor to the present representative, who is unable to serve longer in this capacity.

Committee on Standardized Methods for Vitamin Research.—The committee appointed by the American Chemical Society for the study and possible standardization of methods of investigating vitamin values has held no meeting and recommended no official action during the past year.

Because the whole subject of vitamin investigation is still in such a formative stage, the committee will, doubtless, be slow to make recommendations to the Society for formal adoption of standard methods. At times, however, the existence of the committee seems to serve a useful purpose in proving a sort of clearing house for views on this subject, as, for instance, in connection with the consideration of methods for vitamin A as included in the last revision of the U. S. Pharmacopoeia.

Supervisory Committee on Standard Methods of Analysis.—The report of the Committee on the Analysis of Commercial Fats and Oils has been published in full in *Industrial and Engineering Chemistry*.

The report of the Committee on Coal Sampling and Analysis, covering the methods for determining the fusibility of coal ash, has been accepted by the committee.

It was voted to request the President to appoint a committee of five to be known as the Committee on Coöperation with Industrial Museums. President Rosengarten appointed Marston T. Bogert, *Chairman*, H. E. Howe, William Hoskies, Charles L. Reese, and Gerald L. Wendt.

The Council unanimously voted their appreciative thanks to the Virginia Section; its officials; and the chairman and members of the committees in charge of the Richmond Meeting for their boundless hospitality and unusual attention to the welfare of the members in Richmond. The Secretary was instructed to send the thanks of the Society to the chairman of the committees for the Richmond Meeting and individually

to numerous citizens and organizations of Richmond, a list of whom was furnished him by the local section.

The Council then adjourned.

CHARLES L. PARSONS, *Secretary*

COUNCIL

President Rosengarten has appointed S. W. Parr as the representative of the American Chemical Society on the Sectional Committee on the Classification of Coal of the American Society for Testing Materials.

MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15, 1927

AKRON SECTION

Griffi, George E.
Searight, W. B.
Sellman, Gerald G.
Wianiewski, Marion C.
Woolman, Russell J.

CALIFORNIA SECTION

Beebe, Clarence W.
Henry, Roy
Luck, J. Murray

CENTRAL TEXAS SECTION

Ross, R. S.

CHICAGO SECTION

Dahl, Jacob
Olmsted, Alanson W.
Reitz, William
Worthington, T. T.
Zoller, Miles M.

CINCINNATI SECTION

Henne, Albert L.

CLEVELAND SECTION

Eichelberger, William C.
Kemet Laboratories Co.
Van Dusen, Charles H., Jr.
Ware, John Leroy

COLORADO SECTION

Wiley, Howard Leroy

COLUMBUS SECTION

Brown, Edwin
Reeves, Alpheus O.

CONNECTICUT VALLEY SECTION

Candee, Ellsworth T.

CORNELL SECTION

Newell, John

DETROIT SECTION

Fadgen, Thomas J.

FORT WAYNE SECTION

Picard, Robert F.

FLORIDA SECTION

Carrigan, R. A.

INDIANA SECTION

Cassady, Emil V.
Moseley, W. K.

IOWA SECTION

Poarch, S. D.

KANSAS CITY SECTION

Gray, L. R.
Spalding, James L.

LEHIGH VALLEY SECTION

Klein, Ernest H.
Reinbolt, Emmett B.

MARYLAND SECTION

Cottle, Delmar L.
McKibbin, Reginald R.

MINNESOTA SECTION

Eklund, Carl M.
Olsen, Samuel R.

NEW HAVEN SECTION

Doolan, Leonard W.

NEW YORK SECTION

Chiappe, Caesar Frank
Jackson, David H.
Kimball, Cyril S.
Kurzrok, Raphael
Lloyd, W. Spencer
Morrill, Miss Hester B.
Murphy, John J.
Pearl, Frank A.
Post, Fred
Teichmann, Charles F.
William R. Warner & Co.
Whitaker, John Martin

NORTHEASTERN SECTION

Anderson, James Nicholas
 Burrough, Horace, III
 Coolidge, Thomas B.
 Hurxthal, Lewis M.
 McCann, Marion F.
 Parker, Rienzi B.
 Peskin, Charles
 Smith, George Warren
 Ten Broeck, C. W.

NORTH JERSEY SECTION

The Celluloid Company
 Douthett, O. R.
 Reeves, Burnett A.
 White, William Thomas

OKLAHOMA SECTION

Getschman, Walter E.

PHILADELPHIA SECTION

Britt, Edward F.
 Haun, Oliver
 Kiehel, Stephen R.
 Kimble, Herman K.
 Niekamp, William S.
 U. G. I. Contracting Co.
 Wolff, Wm. A.

PITTSBURGH SECTION

Black, Harold R.
 Call, R. G.
 Lyle, Aaron K., Jr.

RHODE ISLAND SECTION

Sherman, Clarence S.

ROCHESTER SECTION

Quirk, Raymond F.

SACRAMENTO SECTION

Cleveland, Harold

ST. JOSEPH VALLEY SECTION

Studebaker Corporation

ST. LOUIS SECTION

Baltzell, I. M.
 Garibay, Miquel G.
 Doun, Wilson I.
 Vogler, H. A.

SOUTHEASTERN TEXAS SECTION

Brison, William
 Fox, W. E.
 Neuhaus, Max
 Williams, W. Howell, Jr.

SOUTHERN CALIFORNIA SECTION

Bradbury, Norris E.
 Lynam, Charles H.

Soenick, Benj.
 Taylor, Jack Francis M.

UNIVERSITY OF ILLINOIS SECTION

Lausing, William D.

VIRGINIA SECTION

Bailey, William Fleming
 Brown, Warren W.
 Gasser, Helen
 Woodworth, C. C.

WASHINGTON SECTION

Hess, Frank L.

WESTERN NEW YORK SECTION

Dieterle, Paul

WISCONSIN SECTION

Colburn, Allan P.
 Minsart, A. P.
 Rubner, H. H.

NO SECTION

Abitibi Power & Paper Co.
 Agnew, A. Louise
 Alitto, Santo Siciliano
 Beuapre, Hector F.
 Black, C. J.
 Blumenfeld, Joseph
 Burman, Sigurd
 Donker, U. J.
 Hemperly, William F.
 Henri, Victor
 Hughes, John P.
 Hunt, Frank Louis
 Hunter, George
 Johnson, Elmer S.
 Kistiakowsky, George B.
 Kling, Kazimierz
 Larson, Howard
 Leake, Hugh Martin
 Michigan Limestone & Chemical Co.
 Minovici, Stefan
 Mora, Antonio
 Myddleton, William Whalley
 Negoro, Kenzo
 Oberlin, William A.
 Priddy, Richard R.
 Rsaor, Alpha Permelia
 Sansome, Raffaele
 Singer, Leopole
 Sobrinho, A. Menezes
 Spolek Posluchacu Izenyrstvi Chemie
 Stanford, G. Hunt
 Stilwell, R. F.
 Taylor, Roy L.
 Van Es., A. C.
 Vesterberg, Ragnar Olaf Hjalmar
 von der Heide, J. Homan
 Walter, John
 York Oil & Chemical Co.

DECEASED

- Allebach, Theodore H., 120 Quincy St., West Lafayette, Ind. Died, January 11, 1927.
- Base, Daniel, 4105 Alto Ave., Windsor Hills, Baltimore, Md. Died, June 17, 1926.
- Bell, Richard D., 26 Bow St., Somerville, Mass. Died, December 6, 1925.
- Buehlar, Peter Merrie, 223 Elizabeth Ave., Elizabeth, N. J. Deceased (no date given).
- Casale, Luigi, 9 via Parlamento, Roma, Italy. Died, February 18, 1927.
- Chamberlain, W. E. Bureau of Printing and Engraving, Washington, D. C. Died, January 18, 1927.
- Congdon, Charles C., Engineering Lab., C. I. P. S. Co., Springfield, Ill. Died, April 28, 1926.
- Crossley, Arthur W., Shirley Institute, Didsbury, Manchester, England. Deceased (no date given).
- Curme, Henry R., c/o Savell, Sayre & Co., Inc., Niagara Falls, N. Y. Died, Mar 16, 1927.
- Englehardt, H., 2912 Garrison Ave., Forest Park, Baltimore, Md. Died, February 9, 1927.
- Folsom, Herbert A., 88 White St., E. Boston, Mass. Died, January 11, 1927.
- Holmes, Mary Elizabeth, Connecticut College, New London, Conn. Died, Mar 12, 1927.
- Hortvet, Julius, Old Capitol, St. Paul, Minn. Deceased (no date given).
- Hueber, Harry, 85 Warren St., Newark, N. J. Died, February 2, 1927.
- Klain, Joshua J., 5221 Diamond St., Philadelphia, Pa. Died, September 29, 1926.
- Lahey, John A., Seward, N. J. Died, January 13, 1927.
- Levy, Benita, 67 Willow Ave., Hackensack, N. J. Deceased (no date given).
- Markell, Geo. W., Hercules Powder Co., Wilmington, Del. Deceased (no date given).
- Melgar, J., 9a Calle Oriente No. 1, Guatemala, Rept. De Guatemala, Central America. Died, February 6, 1927.
- Meschenmoser, William F., New Dorp, S. I., N. Y. Died, March 16, 1926.
- Power, Frederick B., Bureau of Chemistry, Washington, D. C. Died, Mar 26, 1927.
- Remsen, Ira, Johns Hopkins University, Baltimore, Md. Died, March 4, 1927.
- Roessler, Franz, 89 High St., Perth Amboy, N. J. Died, March 24, 1926.
- Smith, Albert W., 11,333 Bellflower Ave., Cleveland, Ohio. Died, March 4, 1927.
- Smith, C. G., 505 North Sixth St., Canon City, Colo. Died, March 5, 1927.
- Vesterberg, Karl Albert, Stockholms Hogskola, Stockholm, Stockholm, Sweden. Died, Jan 21, 1927.
- Walker, J. Harold, 721 Kansas City St., Rapid City, S. Dak. Deceased (no date given).
- Wesener, J. A., 200 E. Pearson St., Chicago, Ill. Died, November 18, 1926.
- Yoshikawa, Tamakichi, c/o Hammanatsu Tech. College, Hammanatsu City, Japan. Died, August 28, 1925.
- Young, Robert H., 808—145th St., East Chicago, Ind. Deceased (no date given).
- Zdanowich, J. O., 36 St. James Street, London, S. W. 1, England. Died, December 31, 1926.

SCINNATI . .

Proceedings

COUNCIL

President Rosengarten has appointed Herman Schlundt as the representative of the American Chemical Society at the Centennial Celebration of Lindenwood College, St. Charles, Missouri, May 30, 1927.

MEMBERS ELECTED BETWEEN APRIL 15 AND MAY 15

AKRON SECTION

Cosler, V. A.

ARIZONA SECTION

Hastings, James W.

CALIFORNIA SECTION

Greene, Roger S.

Lindsay, Harold W.

Meyers, Harold J.

Miller, Marvin F.

Montgomery, Montel

Rose, Carlton H.

CENTRAL PENNSYLVANIA SECTION

Calvert, John B.

Schaefer, Wilton E.

CENTRAL TEXAS SECTION

Green, Carroll

Petty, Marvin L.

CHICAGO SECTION

Brown, Eugene P.

Clark, John T.

Fdee, R. Herbert

Engler, Joseph S.

Jameson, Albert R.

Kohn, Herbert

Noren, Laurence E.

Svarnas, Anastus Anthony

Vaughn, William Edward

CLEVELAND SECTION

Kerr, E. G.

Lieben, Eugene William

COLORADO SECTION

Sellers, J. E.

COLUMBUS SECTION

Hyatt, Charles S.

Williams, Rine

INDIANA SECTION

Moraw, Harry O.

Short, W. F.

Weger, W. R.

IOWA SECTION

Blackman, Leslie Everett

KANSAS CITY SECTION

Foster, E. R.

Paulsen, Henry C.

Weimer, S. H.

LOUISIANA SECTION

Flynn, Francis F.

Heideman, A. G.

MINNESOTA SECTION

Wilson, Gordon C.

NASHVILLE SECTION

Epstein, Edward

NEW HAVEN SECTION

Hamilton, Schuyler

Schwartz, Emil W.

NEW YORK SECTION

Bitter, J. L.

Chalupski, Victor

Chisdes, Meyer

Crosby, George W.

Dorion, O. R.

Dunn, Clarence S.

Pliegel, Hilda C.

Gustus, Edwin Lysle

Ileyman, Wilbert A.

NORTH CAROLINA SECTION

Fox, Etrol L.

NORTHEASTERN SECTION

Dole, Malcolm

Gill, Jack E.

Gohr, Edwin J.

Happel, John

Peterson, Ralph F.

Warren, Thomas E.

NORTH JERSEY SECTION

Bostwick, Mary V.

Chamberlin, C. L.

Hanson, Norman D.

Herzog, Joseph V.

Hoffman, Harry A.

Kunzenbacher, August A.

O'Neill, John F.

Peakes, Gilbert L.

Riley, Horace E.

Taylor, Thomas Smith
White, Robert
Yanowski, Leo, K.

NORTHERN LOUISIANA SECTION
Griffin, Harden T., Jr.

NORTHERN WEST VIRGINIA SECTION
Beck, John

OHIO NORTHERN SECTION
Ohio Sugar Company, The
Wood, Harold G.

OKLAHOMA SECTION
Thompson, Warren L.

OREGON SECTION
Struthers, William A.

PHILADELPHIA SECTION
Brehm, Joseph R.
Jacobs, Adeline H
Karchuta, M. C.
Meyer, Julius W.
Obold, Walter Lord
Smith, Leighton K.

PITTSBURGH SECTION
Bartholomae, Barth Edgar
Gray, Dan. M.
Harper, L. E.
Offutt, Harold H.

PUGET SOUND SECTION
Colman, Isabel S.

RHODE ISLAND SECTION
Hollingworth, D. W.

SACRAMENTO SECTION
Kirk Geary & Co.

ST. JOSEPH VALLEY SECTION
Benning, A. F.
Foosey, William L.
Mahin, William E.

ST. LOUIS SECTION
Heath, George M.
Marschuetz, Howard H.
Taylor, Russell L.
Thummel, W. G.

SOUTH JERSEY
Berger, Ernst, K. H.

SOUTHEASTERN TEXAS SECTION
Chapman, T. S., Jr.

SOUTHERN CALIFORNIA
Coepland, John D.
St. Clair, Robert W.
Seaman, Alfred K.

UNIVERSITY OF ILLINOIS SECTION
Pauley, Gerald F.
Pearson, E. L.

UNIVERSITY OF MICHIGAN SECTION
Wagner, Arthur M.
Zack, Vladimir P.

VIRGINIA SECTION
Dearing, A. Willis
Dodson, A. M.

WASHINGTON, D. C. SECTION
Harriman, Arthur J.
Schulte, George N.

WESTERN NEW YORK SECTION
Clayton, Herbert W
Sharples, William Charles

NO SECTION
Barton, J. Frank
Bond, George W.
Bonner, James N.
Borbeck, Perry Landis
Buchner, Max
Burbacher, John Jacob
Dahlstrom, Karl Erik
Danaila, N.
Dodge, Arthur C.
Hardy, A. Eugene
Hopkins, Paul
Kimbrell, Robert W.
Lambiotte, Auguste
Lewis, F. M.
Ludwig, Edward H.
Manchot, W.
Odagiri, Mizuo
Roth, Pedro
Saddington, Arthur Ward
Sinclair, Murray
Soherr, Will
Westfall, Benton B.

Proceedings

COUNCIL

President Rosengarten has appointed J. E. Mills as the representative of the American Chemical Society on the Sectional Committee of the National Safety Council for a Safety Code on Colors for the Identification of Gas Mask Canisters.

LIST OF MEMBERS ELECTED BETWEEN MAY 15 AND JULY 15, 1927

AKRON SECTION

Eberhart, Dale R.
Kern, Ervin S.
Washburn, C. R.

CALIFORNIA SECTION

Beliaeff, Nicolai N.
Leicester, Henry M.
McKenna, Philip M.
Wood, Dennistoun, Jr

CHICAGO SECTION

Hayson, Frank M.
Hessle, Eric Th.
Hoen, R. E.
Liebl, Florence I.
Lyon, Alice L.
Mayser, Richard D.
Miller, Herbert J.
Parkhurst, George L.
Place, Muriel E.
Snyder, Verne D.

CINCINNATI SECTION

Lurie, Jacob

CLEVELAND SECTION

Craytor, Morgan Wells
Gibbons, Gilbert P.
McGean, Ralph L.

COLORADO SECTION

Heckman, Russell F.
Ober, Aaron G.

COLUMBUS SECTION

Owens, Charles Robley

DETROIT SECTION

Heyn, Myron

GEORGIA SECTION

LeConte, Joseph N.

IOWA SECTION

Snyder, Robert G.

KANSAS CITY SECTION

Coventry, Margaret

LOUISIANA SECTION

Danneker, John Martin

MARYLAND SECTION

Dobler, George G.
Leatherman, Martin

MICHIGAN STATE COLLEGE SECTION

Evans, Hubert E.

NEW YORK SECTION

Bitler, William Peter
Denzler, Harry Louis
Hoskins, Fred T.
Inman, Marcus Tullius, Jr.
Kellogg, Minerva
Marks, Lewis Hart
Park, George C.
Price, Richard J.
Robinson, Arthur Milton
Sullivan, Dennis E.
Torigian, John

NORTH CAROLINA SECTION

Bullitt, James B., Jr
Clifford, Alfred T.

NORTH JERSEY SECTION

Greene, Mildred C.
Holder, G. C.
Thatcher, Frederick M.
Warner, C. W.

NORTHEASTERN SECTION

Cox, Verna E.
Gustafetti, Joseph A.
Pedersen, Charles J.
Poland, George L.
Shepard, David A.

NORTHWESTERN UTAH SECTION

Willits, Charles O.

OKLAHOMA SECTION

Colby, M. G.
Russell, J. T.

PHILADELPHIA SECTION

Barba, Milton B.
Barker, Walter C.
Mitchell, Clinton K.
Nicholls, Chas. R.
Walker, Henry B.

PITTSBURGH SECTION

Reizenstein, Louis J.

PURDUE SECTION

Gibbons, Robert Charles

ROCHESTER SECTION

Englert, Justin F.

Spengler, John Arthur

SAINT LOUIS SECTION

Kollme, Sidney P.

Spencer, George L.

SOUTHERN CALIFORNIA SECTION

Bechtold, Ira C.

Coffeen, John M.

Donaldson, Wm. E.

Ewing, Fred J.

Johnston, Genevieve E. M.

Murray, H. T.

Whistler, Arthur McLeod

UNIVERSITY OF ILLINOIS SECTION

Puntambeker, Shripati V.

UNIVERSITY OF MICHIGAN SECTION

Ho, Kai

Stapleton, Chester B.

VIRGINIA SECTION

Strother, Bryant L.

WASHINGTON SECTION

Tener, Rees F.

WEST NEW YORK SECTION

Munro, Albert E.

Stevens, W. H.

NO SECTION

Beresford, Ewart

Brazier, Sidney Albert

Buchan, John E.

Cavett, Jesse William

Chemical Department of Cairo

Daroon, Phra

Fenton, James George

Frye, A. L.

Gurd, George W.

Hastilow, C. A. F.

Lombardo, Francisco Diaz

McGowan, & Sons, Inc., P. J.

McNulty, Catherine E.

Meyers, Jos. E.

Newman, Edwin Stuart

O'Shaughnessy, F. R.

Peacock, William

Rhoads, Ralph George

Roderick, Donald Barclay

Saxon, Robert

Secor, Herbert W.

Waeser, Bruno

Wischer, Paul

DECEASED

Culmann, J. G. Edward, Lock Haven, Pa. Died June 12, 1927.

Darby, Edward H., Rome, N. Y. Died June 11, 1927.

Lenger, Victor, 1718 Summit Ave., Madison, Wis. Died June 14, 1927.

Lovenberg, H. A., 113 Oak Ave., Ithaca, N. Y. Died Nov. 29, 1926.

Mabery, C. F., Congress Square Hotel, Portland, Me. Died June 26, 1927.

Sligh, T. S., Jr., Studebaker Corp., South Bend, Ind. Died March 30, 1927.

Stephenson, Frank T. F., 4815 Trumbull Ave., Detroit, Mich. Died May 14, 1927.

Proceedings

GENERAL MEETING MINUTES

The Seventy-fourth General Meeting of the American Chemical Society was held at the Statler Hotel, Detroit, Michigan, from Monday, September 5 to Friday, September 9, inclusive.

A full account of the meeting will be found in the News Editions of *Industrial and Engineering Chemistry* for September 10 and 20.

The Council meeting was held on the afternoon of September 5. On Monday evening there was also a formal reception and dance at the Hotel Statler.

Four general divisional meetings were held on Tuesday afternoon and divisional meetings on Wednesday, Thursday morning and Friday morning, as outlined in the News Edition for August 20.

The boat ride on the Detroit River on Tuesday evening with approximately a thousand present was thoroughly enjoyed, the occasion being enlivened by music, dancing, bridge and other amusements.

On Wednesday evening President Rosengarten, at the Cass Technical High School, presented his annual address entitled "Reflections." This was followed by an address by Charles F. Kettering on "The Functions of Research," both of which will be published in *Industrial and Engineering Chemistry*.

The registration showed 1618 members and guests present.

On Thursday evening a special feature entertainment enlivened by vaudeville performers, dancing, music, etc., filled the ballroom of the Statler Hotel to overflowing. On Thursday afternoon and Friday numerous trips were arranged to industrial establishments in Detroit and to the University of Michigan at Ann Arbor.

A special ladies' program, already printed, was a feature of the meeting.

All divisions of the Society met in divisional meetings, details of which, as well as of numerous social gatherings, including luncheons and dinners of affiliated groups, will be described in the News Edition and in the regular edition of *Industrial and Engineering Chemistry*.

The divisions elected officers as follows. These will be found regularly published in the opening pages of each issue of the *Journal of the American Chemical Society*.

BIOLOGICAL: Chairman, Paul E. Howe; Secretary, M. X. Sullivan; Executive Committee, H. B. Lewis, A. P. Lothrop, Icie G. Macy, J. R. Murlin, H. A. Shoule, S. D. Wilkins.

CELLULOSE: Chairman, L. E. Wise; Vice-Chairman, J. L. Parsons; Secretary, E. C. Sherrard; Executive Committee, H. LeB. Gray, B. Johnsen.

CHEMICAL EDUCATION: Chairman, B. S. Hopkins; Vice-Chairman, H. R. Smith; Secretary, R. A. Baker; Assistant Secretary, L. J. Wood; Treasurer, E. M. Billings; Executive Committee, L. W. Mattern, Wm. McPherson, W. Segerblom.

COLLOID: Chairman, H. B. Weiser; Secretary, F. E. Bartell; Executive Committee, W. D. Bancroft, R. H. Bogue, R. A. Gortner, W. D. Harkins, H. N. Holmes, J. H. Mathews, S. E. Sheppard, E. B. Spear.

DYE: Chairman, M. L. Crossley; Vice-Chairman, E. K. Bolton; Secretary-Treasurer, H. T. Herrick; Executive Committee, C. G. Derick, L. A. Olney.

FERTILIZER: Chairman, E. W. Magruder; Vice-Chairman, Wm. H. Ross; Secretary, H. C. Moore; Executive Committee, J. E. Breckenridge, H. R. Kraybill, E. W. Magruder, A. R. Merz, H. C. Moore, A. J. Patten, Wm. H. Ross.

- GAS AND FUEL:** Chairman, A. C. Fieldner; Vice-Chairman, S. P. Burke; Secretary-Treasurer, O. O. Malleis; Executive Committee, G. G. Brown, R. S. McBride.
- HISTORY OF CHEMISTRY:** Chairman, Lyman C. Newell; Secretary, Tenney L. Davis; Executive Committee, C. A. Browne, Geo. L. Coyle, F. B. Dains.
- INDUSTRIAL & ENGINEERING CHEMISTRY:** Chairman, R. J. McKay; Vice-Chairman, R. E. Wilson; Secretary-Treasurer, E. M. Billings; Executive Committee, T. A. Boyd, Jr., J. Bennett Hill, W. J. McAdams, Walter Schmidt, J. R. Withrow.
- LEATHER AND GELATIN:** Chairman, Arthur W. Thomas; Vice-Chairman, Frank L. DeBeukelaer; Secretary-Treasurer, August C. Orthmann; Executive Committee, Norman C. Hertz, S. E. Sheppard.
- MEDICINAL CHEMISTRY:** Chairman, A. W. Dox; Vice-Chairman, Frederick Fenger; Secretary-Treasurer, A. E. Osterberg.
- ORGANIC:** Chairman, William Lloyd Evans; Secretary-Treasurer, F. C. Whitmore.
- PAINT AND VARNISH:** Chairman, W. T. Pearce; Vice-Chairman, P. E. Marling; Secretary-Treasurer, E. W. Boughton; Executive Committee, J. S. Long, J. R. MacGregor.
- PETROLEUM:** Chairman, J. B. Hill; Vice-Chairman, F. W. Padgett; Secretary-Treasurer, Carl L. Johnson; Executive Committee, C. O. Johns, R. R. Matthews.
- PHYSICAL AND INORGANIC:** Chairman, George L. Clark; Vice-Chairman, Victor K. LaMer; Secretary-Treasurer, Ward V. Evans; Executive Committee, G. S. Forbes, J. H. Hildebrand, W. H. Rodebush, H. S. Taylor, H. B. Weiser.
- RUBBER:** Chairman, H. L. Fisher; Vice-Chairman, Arnold H. Smith; Secretary-Treasurer, H. E. Simmons; Executive Committee, E. R. Bridgewater, J. M. Fry, Stanley Krall, W. G. Nelson, H. A. Winkelmann.
- SUGAR:** Chairman, F. J. Bates; Secretary-Treasurer, F. W. Zerban; Executive Committee, J. F. Brewster, D. L. Davoll, H. I. Knowles, W. B. Newkirk, S. J. Osborn, J. W. Schlegel.

CHARLES L. PARSONS, *Secretary*

DIRECTORS' MINUTES

The Directors of the American Chemical Society met in the Statler Hotel, Detroit, Michigan, Monday, September 5, 1927, at 8 P.M., with President George D. Rosengarten in the chair and Messrs. W. D. Bancroft, W. D. Bigelow, S. W. Parr, Charles L. Parsons and John E. Teeple present.

The rate schedule for reprints as tabulated and already put in force by Editor Lamb was approved by the Directors as follows:

No. copies	REPRINTS PER PAGE		Covers
	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 8 pp. or less per page	9 pp. or more per page	
50	\$.20	\$.14	\$1.77
100	.32	.24	2.05
150	.45	.33	2.33
200	.51	.42	2.60
250	.59	.50	2.88
300	.67	.58	3.16
350	.76	.66	3.43
400	.84	.74	3.71
450	.92	.82	3.99
500	1.00	.90	4.26
550	1.08	.98	4.54
600	1.16	1.06	4.82
650	1.24	1.14	5.10
700	1.31	1.21	5.37
750	1.39	1.29	5.65
800	1.47	1.37	5.93
850	1.55	1.45	6.20
900	1.62	1.52	6.48
950	1.71	1.60	6.76
1000	1.71	1.60	7.03
Extra M's.	1.14	1.14	6.71

The request of Editor E. J. Crane for an additional allotment of \$3,050 for the 1927 budget of *Chemical Abstracts* was granted with instructions to the Treasurer to transfer any available income of the Endowment Fund toward meeting this appropriation, taking the balance from current funds of the Society.

The Treasurer reported the following transactions since the last Directors' meeting, which were duly approved:

1. The sale of \$1900 par value First, Third and Fourth Liberty Bonds, net of \$1978.85 from Decennial Index Fund.
2. The receipt of a check for \$250.00 from the Virginia Section, in June 1927, for the Endowment Fund.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*

EXECUTIVE COMMITTEE MINUTES

The Executive Committee met in Parlor A of the Statler Hotel, Detroit, Michigan, at 2 o'clock, Sunday, September 4, 1927, with President Rosengarten in the chair and Messrs. A. M. Comey, E. J. Crane, H. E. Howe, Wm. McPherson, S. W. Parr, Charles L. Parsons and John E. Teeple present.

The Committee considered the resolution referred to them at the Richmond Meeting covering the establishment of an Institute of Chemical Education and formulated a report to the Council which will be found printed in the Council proceedings of September 5.

President Rosengarten having asked the advice of the Executive Committee covering a request from the American committee for participation in the international "Maison de la Chimie" for the use of his name as a member of the Committee, it was voted that it was their unanimous opinion that he should decline the use of his name and influence on the basis that his acceptance would tacitly commit the American Chemical Society to a procedure it could not approve. The full vote with reasons therefor will be found in the Council proceedings of September 5, it having also been unanimously adopted by the Council.

The Committee having requested the Directors of the Society to meet with them, the above personnel was increased at 3 o'clock by Directors W. D. Bigelow and W. D. Bancroft, and the situation regarding the relation of the Society to the Division of Chemical Education and the *Journal of Chemical Education* was discussed. As the Executive Committee of the Division of Chemical Education was also in session the meeting adjourned to await their deliberations.

The Directors and the Executive Committee met again at 10 o'clock on the morning of September 5 and after receiving the report of the deliberations of the Executive Committee of the Division of Chemical Education, as made to the President and the Secretary the previous evening, the entire body voted as follows:

"That the Executive Committee and Directors in joint sessions are unanimously appreciative of the attitude of loyalty to the Society shown by the Executive Committee of the Division of Chemical Education in their conference with the President and the Secretary on the evening of September 4, as reported to us; express our realization of the good work of their Division in the cause of chemical education; recognize fully the importance of that work to the cause of American chemistry, and pledge their best endeavors to enable the Division to publish the *Journal of Chemical Education* under their control and auspices."

It was also unanimously voted to approve the acts of the President and the Secretary in connection with the relation of the Division of Chemical Education to the

American Chemical Society, as contained in the correspondence with the officers of the Division from April 25, 1927, to August 5, 1927, inclusive.

The Committee then adjourned.

CHARLES L. PARSONS, *Secretary*

COUNCIL MINUTES

The meeting of the Council of the American Chemical Society was called to order by President George D. Rosengarten at 2 P.M. on Monday, September 5, 1927, in the Statler Hotel, Detroit, Michigan, with the following councilors and substitutes present:

Ex-Officio.—W. D. Bancroft, W. D. Bigelow, F. B. Carpenter, E. J. Crane, M. L. Crosley, F. B. Dains, R. P. Dinsmore, Geo. Shannon Forbes, Charles H. Herty, B. S. Hopkins, H. F. Howe, E. F. Kohman, S. W. Parr, Charles L. Parsons, Edgar P. Smith, John E. Teeple, John Arthur Wilson.

Councilors at-Large.—Roger Adams, Erle M. Billings, A. M. Comey, Harlan S. Miner, Frank C. Whitmore.

Local Sections.—*Alabama*, John R. Sampey (subs. for B. B. Ross). *Ames*, F. E. Brown (subs. for W. F. Coover). *California*, Robert N. Wenzel (subs. for C. L. Alsborg). *Central Pennsylvania*, E. D. Ries. *Chicago*, H. E. Barnard, W. V. Evans (subs. for Wm. Hoskins, Sr.), D. K. French, Paul N. Leech (subs. for Paul Van Cleeft), S. L. Redman (subs. for David Klein), W. R. Smith, E. H. Volwiler, H. G. Walker, Robert E. Wilson. *Cincinnati*, L. W. Bosart (subs. for G. D. McLaughlin), F. C. Broeman (subs. for C. R. Bragdon). *Cleveland*, Hippolyte Gruener, J. D. Morron, O. F. Tower. *Colorado*, R. G. Gustavson (subs. for L. D. Roberts). *Columbus*, Wm. McPherson. *Cornell*, A. W. Browne. *Delaware*, Cole Coolidge (subs. for Charles L. Reese). *Detroit*, H. C. Hamilton, George W. Winchester. *Erie*, John L. Parsons (subs. for Charles H. Reese). *Fort Wayne*, Eskel Nordell. *Georgia*, J. Samuel Guy (subs. for Thomas C. Law). *Illinois-Iowa*, O. K. Smith. *Indiana*, Edgar B. Carter. *Iowa*, L. Chas. Raiford. *Louisiana*, C. E. Coates. *Maine*, C. A. Brautlecht. *Maryland*, E. Emmet Reid. *Michigan State College*, Arthur J. Clark. *Midland*, William J. Hale. *Milwaukee*, A. C. Orthmann. *Minneapolis*, E. P. Harding (subs. for M. C. Sneed), G. H. Montillon (subs. for C. H. Bailey). *Nebraska*, B. Clifford Hendricks (subs. for F. W. Upson). *North Jersey*, C. O. Johns, A. V. H. Mory (subs. for J. G. Lipman). *New York*, S. P. Burke, C. R. Downs, C. M. Hoke (subs. for T. B. Freas), William Haynes (subs. for Martin H. Ittner), James Kendall, D. H. Killefer, Charles A. Lunn, R. R. Renshaw, Foster Dee Snell, S. D. Swan (subs. for H. B. Lowe), Arthur W. Thomas, M. C. Whitaker (subs. for B. T. Brooks), Lois W. Woodford (subs. for Marie Reimer), F. W. Zerbahn (subs. for H. R. Moody). *North Carolina*, A. S. Wheeler. *Northeastern*, C. R. Boggs (subs. for W. L. Jennings), G. J. Esselen, Jr., Arthur J. Hohman, Arthur D. Holmes, Robert W. Neff, Wilhelm Segerblom. *Northern West Virginia*, A. R. Collett (subs. for C. A. Jacobson). *Omaha*, L. B. Parsons (subs. for Wm. Harr). *Philadelphia*, J. Bennett Hill, Henry S. Lukens, J. Spencer Lucas, Joseph Rosin (subs. for C. S. Hinton), O. L. Shinn (subs. for Horace C. Porter), Walter T. Taggart, James G. Vail (subs. for Wm. Stericker). *Pittsburgh*, J. H. James, Alexander Silverman. *Princeton*, Robert N. Pease (subs. for C. P. Smyth). *Purdue*, R. E. Nelson. *Rhode Island*, N. W. Rakestraw (subs. for R. F. Chambers). *Rochester*, E. K. Carver (subs. for Hans T. Clarke). *Saint Joseph Valley*, J. A. Nieuwland. *Saint Louis*, T. R. Ball. *Southeastern Texas*, Harry B. Weiser. *Southern California*, Walter A. Schmidt. *South Jersey*, R. E. Rose. *Syracuse*, R. A. Baker. *Toledo*, George H. Anderson. *University of Illinois*, A. M. Buswell, D. B. Keyes. *University of Missouri*, Herman Schlundt. *Vermont*, S. Francis Howard. *Washington*, D. C., L. H. Adams, W. Blum, W. Mansfield Clark, L. E. Warren (subs. for V. K. Chesnut). *Western New York*, V. L. Robinson (subs. for E. R. Riegel), Lester F. Hoyt (subs. for J. A. Handy), F. L. Koethen. *Wisconsin*, L. F. Hawley.

The Council voted to authorize the Section of History of Chemistry to form a Division of History of Chemistry and the following by-laws were adopted:

BY-LAWS OF THE DIVISION OF THE HISTORY OF CHEMISTRY

ARTICLE I

Membership

Membership in the Division shall be open to all members of the American Chemical Society, and any member of the Society shall, upon request to the Secretary of the Division, be registered as a member of the Division.

ARTICLE II

Officers

Section 1. The officers of the Division shall be a chairman, a recording secretary, and an executive committee.

Section 2. The chairman and the secretary shall be members of the Executive Committee ex-officio.

Section 3. The Executive Committee shall consist of three registered members of the Division and the members ex-officio, provided by Section 2 of this article. The chairman of the Division shall be chairman of the Executive Committee.

Section 4. At the first session of the Division coincident with the annual meeting of the Society and following the report of the Secretary, the Chairman shall appoint from the members present at the meeting a committee of three whose duty it shall be to nominate officers for the ensuing year. This committee shall present the list of nominations immediately preceding the election of officers at the last session during that annual meeting.

Section 5. All officers of the Division shall be elected annually by ballot at the last session of the Division held during the annual meeting of the Society, and shall take office at the close of the meeting at which they were elected. They shall hold office for one year or until their successors are elected. Voting by proxy or by letter shall not be allowed.

Section 6. The Executive Committee shall fill any vacancies occurring through death or resignation among officers of the Division.

Section 7. It shall be the duty of the chairman to represent the Division in the Council of the Society, to preside at meetings of the Executive Committee, to carry into effect the decisions and recommendations of that committee, to preside at stated meetings of the Division, and to report to the Society at its regular meetings.

Section 8. It shall be the duty of the recording secretary to keep a record of the proceedings of the Division and of the Executive Committee to maintain a list of registered members, to send to registered members such notices as the business of the Division may require, and to transmit to the Secretary of the Society the names of all the officers and standing committees of the Division within three weeks of their appointment; and, in like manner, to notify the Secretary of the Society of any change of officers or standing committees during the year.

Section 9. The recording secretary shall be the custodian of the files of the Division.

Section 10. The Executive Committee shall conduct the business of the Division and direct its activities. It shall at each general meeting of the Society, and as early as may be, hold a meeting to consider the affairs of the Division and to receive reports of its committees. The voting majority of the Executive Committee shall be responsible for all expenditures which it may authorize, except so far as the action of the Council shall previously have provided for such expenditures.

ARTICLE III

Meetings

There shall be a meeting of the Division at each general meeting of the Society unless for special reason omitted by vote of the Executive Committee. Business affecting the organization of the Division shall be transacted only at the meeting coincident with the annual meeting of the Society.

The order of business shall be as follows:

Reading of minutes.
Report of Executive Committee.
Report of Secretary.
Reports of Committees and discussions.
Reading of papers.
Miscellaneous business.

And at the annual meeting:

Appointment of Nominating Committee.
Report of Nominating Committee.
Election of officers.
Unfinished business.

The regular order of business of the Division may be suspended at any session by the consent of three-fourths of the members present.

ARTICLE IV

Papers

All titles and abstracts of papers and all manuscripts must be in the hands of the recording secretary of the Division on or before the date stated in the preliminary program announcement of each meeting.

ARTICLE V

Assessments

The Executive Committee may at its discretion impose dues not to exceed three dollars (\$3 00) per year upon registered members of the Division, said dues to be collected by the Secretary, and the receipts therefrom to be devoted to the purposes of the Division.

ARTICLE VI

Amendments

These by-laws may be amended at any annual meeting of the Division by a three-fifths vote of the registered members present, provided two weeks' notice of the proposed amendment with the text thereof has been sent to the registered members of the Division. Amendments to be effective must be approved by the Council and accepted by that body as not inconsistent with the constitution and by-laws of the Society.

The Division of Chemistry of Medicinal Products submitted new by-laws somewhat changed from their old by-laws and changing the name of the Division to the "Division of Medicinal Chemistry." The by-laws were duly approved as follows:

BY-LAWS OF THE DIVISION OF MEDICINAL CHEMISTRY

ARTICLE I

Name and Object

Section 1. This Division shall be known as the Division of Medicinal Chemistry of the American Chemical Society.

Section 2. The objective of this Division shall be the advancement of knowledge of the chemistry and pharmacology of substances used in medicine.

ARTICLE II

Membership

Section 1. Any member of the American Chemical Society may become a member of this Division by requesting the Secretary of the Division to enroll him therein.

Section 2. A member in good standing is one who has been accepted by the Secretary and has paid the yearly dues.

ARTICLE III

Officers

Section 1. The officers of this Division shall be a Chairman, a Vice-Chairman and a Secretary-Treasurer, who shall constitute the Executive Committee,

Section 2. The duties of the Chairman, Vice-Chairman and Secretary-Treasurer shall be those that usually pertain to their positions.

Section 3. The officers shall be elected at the last regular session of the Division held during the annual meeting of the American Chemical Society.

Section 4. At the first session of this Division during an Annual Meeting the Chairman shall appoint a nominating committee of three members in good standing to nominate two candidates for each office of the Division—Chairman, Vice-Chairman and Secretary-Treasurer. The committee shall report at the call of the Chairman.

Section 5. The Chairman of the Division is ineligible for renomination by this Committee.

Section 6. The Executive Committee shall act for the Division in the interim between meetings of the Division and shall have power to fill all vacancies caused by the death, resignation or removal of an officer, and shall perform all other duties assigned thereto.

ARTICLE IV

Meetings

Section 1. Meetings of the Division shall be held at each general meeting of the American Chemical Society, unless cancelled by the Executive Committee for good and sufficient reasons.

Section 2. The order of business at any business meeting shall be:

- a. Reading of minutes of previous meeting.
- b. Report of Executive Committee.
- c. Report of Secretary-Treasurer.
- d. Appointment of Nominating Committee, if required.
- e. Reports of Committees.
- f. Unfinished business.
- g. New business.
- h. Election of officers, if required.

ARTICLE V

Committees

The Chairman shall, with the advice and consent of the Executive Committee, appoint the Nominating Committee and such other standing and special committees as may be authorized by the Division.

ARTICLE VI

Publications

All papers presented to this Division, must, if intended for publication, be submitted to a journal published under the auspices of the American Chemical Society. If the Editor of this journal does not deem the article suitable for publication therein, or wishes to release it, the Secretary shall advise with the author regarding the place of publication.

ARTICLE VII

Papers

Section 1. Every title of a paper submitted for inclusion in the program of any meeting of this Division shall be accompanied by a 100-word abstract of the paper and the name of the laboratory in which the work was done.

Section 2. The Executive Committee may require the full manuscript of a paper before inclusion of the title in the program, if the abstract does not clearly indicate the nature of the paper.

Section 3. Non-members of the American Chemical Society may be placed upon the program of the Division when they are not American chemists, and then only, by vote of the Executive Committee.

Section 4. The time for the presentation of a paper shall be limited to ten minutes and the time for discussion of any paper shall be limited to five minutes. The Executive Committee may extend upon the program the time for the presentation of any paper. The time for discussion of any paper may be extended by vote of the Division. The Executive Committee may provide on the program for formal, prepared discussions of any paper. No paper shall be read from manuscript.

Section 5. The Secretary shall, two weeks before the date of a general meeting, send abstracts of the papers submitted to all members of the Division in good standing.

ARTICLE VIII

Dues

The dues for all members of this Division in good standing shall be one dollar (\$1.00) per year to cover postage and provide for the distribution of Abstracts of papers to be presented.

ARTICLE IX

Amendments

Amendments to these By-Laws may be proposed at any general meeting and shall be voted upon at the next general meeting.

A proposal that a Section of Chemical Economics be organized was discussed and, without formal vote, was referred to the Division of Industrial and Engineering Chemistry, under the auspices of which a symposium will be held, probably at the Swampscott Meeting, to determine the interest of the subject in the hope that it may ultimately lead to the formation of a Section and, later, a Division of the Society.

The following were re-elected for a term of three years, 1928-1930:

A. B. LAMB, Editor JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

E. J. CRANE, Editor *Chemical Abstracts*.

H. E. HOWE, Editor *Industrial and Engineering Chemistry*.

W. A. Noyes, Editor *Scientific Monographs*.
H. E. Howe, Editor *Technologic Monographs*.

F. A. Liddbury, A. D. Little, and C. E. K. Mees were re-elected associate editors of *Technologic Monographs* for the term 1928-1930.

Roger Adams and E. W. Washburn were re-elected associate editors of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

H. S. Taylor and W. A. Patrick were elected the American Chemical Society's representatives on the editorial board of the *Journal of Physical Chemistry* for a term of two years, replacing G. A. Hulett and Irving Langmuir, whose terms expire in December, 1927.

Wm. McPherson was re-elected a member of the Executive Committee of the Council, term to expire in December, 1930.

The Council authorized the establishment of a South Carolina Piedmont Section upon the receipt of the necessary signatures, as required by the Constitution, under definite designation of headquarters, the territory to include that part of the State of South Carolina west of the Counties of Lancaster, Kershaw, Richland, Lexington and Aiken, and including these Counties.

The Council having received an invitation from the Minnesota Section and from the President of the University of Minnesota to hold the 1929 fall meeting in Minneapolis unanimously voted to accept the invitation.

The President of the Society having been asked to lend his name to the national committee being organized to secure the financial participation of the United States in the erection of a "Maison de la Chimie" in Paris, of an international nature, and intended to house the "International Office of Chemistry," the formation of which is being undertaken through diplomatic channels, the President called upon the Secretary to read various documents bearing upon the matter and to give a history of the recent movements looking toward the creation in one of the capitals of Europe of what appeared to be a movement for the international control of chemistry. Following the complete statement, which included the request of the President of the Society for the advice of the Executive Committee, the following action of the Executive Committee was unanimously endorsed by the Council:

President George D. Rosengarten of the American Chemical Society having asked counsel of his advisors regarding a communication from M. Maurice Leon, vice-chairman of the "American Organization Committee for American Participation in a Maison de la Chimie" requesting the use of his name as a member of the committee, the Executive Committee of the Society unanimously advise him to decline for the reason that his acceptance would tacitly commit the American Chemical Society to a project it cannot approve.

The American Chemical Society is glad to honor the name and accomplishments of Marcelin Berthelot and in evidence thereof has appointed two of its own past presidents to represent it at the Centenary Celebration on October 25, 1927. An international "Maison de la Chimie" and "An International Office of Chemistry" nationally conceived with predetermined control and location in Paris is an entirely different matter to which the American Chemical Society cannot give its adherence, even

tution were not assessed upon the rest of the world.

The American Chemical Society believes that if an International Office of Chemistry, having as its object the centralization of influence of chemical science, both pure and applied, is ever deemed desirable or necessary, it should be inspired through cooperative action of the world's scientific chemical organizations and not by governments through political channels.

The American Chemical Society does not approve any world centralization of control of chemistry and believes that the future progress of chemistry can best be served as heretofore by harmonious cooperation of national organizations.

The Society specifically disclaims any discourtesy to the organizers of the present movement but believes the underlying principle to be so detrimental to continued international cooperation that it would be lacking in probity if it did not make its judgment known.

It was voted that the Secretary be directed to inform the State Department and

other governmental departments before whom the question of the "International Office of Chemistry" had been brought of the Society's opinion.

The report of the Committee on the first Institute of Chemistry of the American Chemical Society was presented as follows and accepted with the sincere thanks of the Council to all those who have been active in furthering the interests of this successful experiment:

REPORT OF THE COMMITTEE ON THE INSTITUTE OF CHEMISTRY

To the Council of the American Chemical Society:—

The first session of the Institute of Chemistry of the American Chemical Society was held at Pennsylvania State College July 5 to 29, 1927. It is impossible to give a complete report in small compass because the activities of the four weeks were so numerous and so complex that space is not available. For this reason and because the outstanding events have been fully reported in the News Edition as well as in popular newspaper and magazine press only a summary is herewith presented.

Following discussion between individuals, and on receipt of a guarantee from the Chemical Foundation that funds would be available to pay a part of the expected costs, a proposal for such a session was made to the Executive Committee by Secretary Parsons early in February. After authorization by this Committee President Rosengarten appointed a special committee to have general charge. This is composed of G. L. Wendt, chairman, C. E. K. Mees, C. M. A. Stine, F. C. Whitmore, W. R. Whitney, F. W. Willard and the following members, *ex officio*: George D. Rosengarten, President, Chas. L. Parsons, Secretary, H. E. Howe, director of the news service, B. S. Hopkins, chairman of the Division of Chemical Education, and N. E. Gordon, chairman of the Committee on Chemical Education. The committee met in New York on March 15 and in Wilmington on May 17. The actual management was intrusted to G. L. Wendt as director, F. C. Whitmore as associate director, and A. W. Kenney as executive secretary. The program was arranged by the committee as thus organized, and special features were in the following hands: publicity, Mr. D. H. Killefer; office management and room reservations, Mrs. Marion L. Kenney; housing and commissary, Mr. Gordon Harris; recreation, Mr. Sherwood L. Reeder. In addition to these an office staff of eleven persons was required. The Pennsylvania State College, which had submitted the only invitation for the meeting, agreed to conduct the financial affairs through the offices of the treasurer, the purchasing agent and the comptroller of the college.

The scheduled program contained four main series of meetings: the daily conferences, the public evening lectures, the popular motion pictures, and the intensive courses of study. No detailed comment on these meetings is possible here but all programs have been published in the News Edition of *Industrial and Engineering Chemistry*. The attendance at the conference varied from 81 to 158 with an average of 125. There were 18 public evening lectures, held daily except Saturday and Sunday, at 8 p.m. The entire membership of the Institute was usually in attendance with many others from the college faculty, the summer session students, and residents of the town of State College also present. The attendance varied from 75 to 350 with an average of about 150. The motion picture performances were given at 6:30, preceding the public lectures, on 18 different days with 33 different titles. This feature was relatively of the least interest to the members of the Institute but was popular with the students of the college summer session and the residents of the town. The capacity of the theatre was 375 and it was almost invariably crowded to the doors, with many standing.

The intensive courses of study were scheduled in connection with the summer session of the college. Twenty such courses in advanced chemistry, biochemistry and physics were conducted by the Institute and 24 additional more elementary courses in the college summer session were open to Institute members, so that 44 different courses were announced. While the average number taking these courses for credit was only about five, due to the small number to whom this feature appealed, the attendance at all courses was much larger. Most members of the Institute even if present for only a week or even a day, made a habit of attending the lectures in these courses regularly and leaving no hour of the day free. Many of the courses therefore regularly had audiences of thirty to fifty, largely composed of transients.

A total of 415 persons registered for the Institute, of whom 29 were of the Pennsylvania State College. The membership, exclusive of invited speakers, represented all portions of the country from New Hampshire and Porto Rico to California and Washington. There was about an equal division between industrial and academic interests represented. The average period of attendance was about 8 days so that the average number present throughout the four weeks was 125.

With so varied and enthusiastic a membership the activities outside the schedule were almost numberless. A partial list would include—exhibits and demonstration lectures by a number of industrial firms; special informal lectures by Dr. F. C. Whitmore; on the atom and the benzene ring, informal games and organized tournaments in golf, tennis, bridge and chess, informal parties at fishing, swimming, mountain hikes, automobile tours, baseball; pretzels and punch in one of the fraternity houses every evening at nine; a daily mimeographed newspaper with gossip and announcements of the program for the following day; organized automobile tours to the Priestley home and grave at Northumberland, Pa., to Penn's Cave and Woodward's Cave, and to Livonia; a special afternoon conference on the Institute itself, for criticisms and suggestions; a "Simp-odium," or mock conference on "The Contribution of the X-Ray to the Pretzel-Benders' Problem," conducted by the younger members on the last evening of the four-week session; a reception for President and Mrs. Rosengarten on the opening night and At-Homes every Sunday on the lawn of the director; several informal dances, a "Children's" masquerade party; and those earnest discussions of chemistry and everything else by small groups far into the night.

Because of the lack of adequate hotel facilities in State College the Institute rented six of the large new fraternity houses adjoining each other on "Locust Lane" and operated them to furnish living quarters for the membership. Undoubtedly the community life thus made possible was the most important single item in the success of the Institute. During the sessions on catalysis these proved inadequate and the chapter house of the Alpha Chi Sigma fraternity was thrown open to take care of the overflow. The kitchens and dining rooms were operated in three of the houses. One house was reserved for women and one for married couples. Married people with children were provided accommodations in furnished houses or with residents of the town.

While some 7000 printed announcements were distributed, hundreds of mimeographed letters were sent to college and industrial executives, posters were sent to several hundred colleges, and articles were written for general and technical journals, the chief reliance for publicity was on the A. C. S. News Service through the News Edition and especially through the daily press. The response of the press

was most gratifying and included not only a very general publication of the news releases in all parts of the country but also frequent editorial comment, news photographs and at least one Sunday rotogravure photograph. No attempt was made to collect newspaper clippings but many hundreds were nevertheless received which show that very few, if any, scientific meetings have had such continued and widespread publicity. National journals such as *Time*, the *Outlook*, *The Literary Digest*, and the *Nation* gave frequent comment on the news from the Institute. The publicity staff prepared 47 special news releases for the daily press, every one of which was widely used. These were kept on file and at the end of the session 26 sets were sold at a price of \$5.00. It is significant that orders for these transcripts included foreign sources.

The demand for the publication of papers delivered at the Institute has been so great that efforts will be made to publish them as an annual volume.

Two speakers were present, on invitation, from England and one from Germany. They were extraordinarily successful in creating international good will and built friendships that went far beyond personalities.

The original budget of the Institute called for an expenditure of about \$15,000 on an expected income of about \$10,000. The accounts are not yet finally closed (August 31, 1927) but only minor items remain which will not exceed \$200 in expenditures nor \$50 in receipts. The balance sheet as of this date shows that while the estimate of receipts was nearly correct the expense far exceeded expectations. Total receipts amounted to \$10,287.67, while the total expenditures were \$23,698.26. This leaves a deficit at present of \$13,410.59.

TABLE OF INCOME AND EXPENDITURES
(As of August 31, 1927)

Program Account		Expenditures	
Receipts			
From Fees	\$3,298.25	Academic Salaries	\$9,530.00
Sale of News Releases	105.00	Administrative Salaries	4,375.78
Sale of Equipment and Surplus supplies	327.47	Office Rent	160.00
TOTAL	\$3,730.72	Theatre Rent	300.00
		Postage	202.27
		Telephone and Telegraph	313.25
		Office Supplies	443.96
		Printing	766.33
		Travel	301.39
		Furniture and Equipment	267.72
		Freight and Express	68.46
		Miscellaneous	117.74
		TOTAL	\$16,846.00
		Deficit	\$13,116.18
Housing and Commissary Account		Expenditure	
Receipts			
Room Rent	\$2,315.25	Salaries and Wages	\$1,720.00
Board	4,241.70	Rent of Houses	2,438.23
TOTAL	\$6,556.95	Supplies	2,693.13
		TOTAL	\$6,851.36
		Deficit	\$294.41
Total Receipts	\$10,287.67	Total Expenditures	\$23,698.26
		Total Deficit	\$13,410.59

The 4.4% loss in the housing and commissary account is due primarily to the wide fluctuation in attendance which necessitated renting the houses for the entire period though some were used for only a brief period, and to the impossibility of anticipating the attendance for any single day, which caused waste in the kitchens. The large deficit in the program account seems inevitable since fees cannot be materially raised. Even without academic salaries, i. e., without the staff of lecturers who gave courses throughout the session, the receipts in this account are \$3,586.18 less than the purely administrative expenses, i. e., the fees provided less than half the administrative expenses and none of the academic. Both of these items, however, can probably be reduced in subsequent sessions and a larger attendance will increase the receipts without increasing the expenditures materially.

G. L. WENDT, Chairman

The following by-law, having been duly presented under constitutional requirements, was unanimously adopted by the Council:

By-Law 23. The Endowment Fund of the Society shall, under Article 4, Sec. 2, of the Constitution of the Society, be collected and administered in two parts: (1) a Permanent Fund, the income of which alone may be expended only to help meet the Society's constantly growing needs for funds to record the results of chemical research in its publications; and (2) a Revolving Fund limited to \$100,000 to insure the publication of successive decennial general indexes to *Chemical Abstracts*, the sales of which shall be credited to the fund until the \$100,000 has been reached or replenished. Any excess above \$100,000 in the Revolving Fund at the end of any fiscal year may be used for the same purposes as the income of the Permanent Fund.

The Executive Committee having had referred to it at Richmond a proposal that an Institute for Chemical Education be established reported as follows, and the report was referred to the Society's Committee of Chemical Education:

At the Richmond meeting the Council referred to the Executive Committee for consideration and report the recommendation of the Committee on Chemical Education that there be approved an Institute for Chemical Education. Although the resolution specifies that in all financial details such an Institute shall be subject to final approval by the Directors and in other matters to the approval of

the Executive Committee or the Council, the committee feels that as referred to it details concerning such an Institute are as yet too nebulous to enable intelligent action to be taken. While it is understood that the discussion of such a research institute, both in the Senate of Chemical Education and in the Committee on Chemical Education, centered around the tentative plan published in the *Journal of Chemical Education* in January, 1927, it has been stated in conversation by several members both of the Senate and of the Committee, that there is a lack of agreement with respect to the plan published. However, resulting discussion has brought forward several points worthy of further consideration.

Therefore, while the Executive Committee feels that the matter is not in a form sufficiently definite to enable it to give either a negative or affirmative answer, it has seemed best to present in this report to the Council a suggestion for the initiation of work in which we are all interested, with the recommendation that the Committee on Chemical Education give it careful study and consideration, with the hope that from it will come a more definite plan upon which the Council and the Directors can take action.

In common with the teaching of other subjects, instruction in chemistry involves content and method. As compared with other subjects, particularly other sciences, the content of chemistry would seem to differ from them more than the method of teaching and since it is always wise to initiate new enterprises with ample caution, the committee feels the Society would only be justified in centering its attention on the content phase of the problem.

Just as it is recognized that accounts of progress in the field of chemistry must be interpreted to the lay public and to the chemists themselves if their work chances to fall outside the given specialty, so it must be recognized that this material seldom appears in a form which makes it easy for the busy teacher, particularly in high and secondary schools, to assimilate it and further interpret it to classes. Even if originally presented in a form suitable for such use, there is generally a considerable period during which authorities disagree and the teacher is at a loss to know which point of view is accepted by the majority of those competent to judge. It is also true that many secondary school teachers have little time in which to read sufficiently widely or to attend the scientific meeting necessary to maintain a broad view of chemistry as it develops, and they gradually become less efficient in the presentation of the subject to succeeding classes.

It is felt therefore that some agency which might be styled, for example, Bureau for Promotion of Chemical Education, might be established primarily for the purpose of presenting in a form most useful to teachers those new theories, principles, and results of investigations upon which there is a fair consensus of opinion, summaries of the status of advance in special lines of chemistry, and specially prepared accounts of the latest discoveries considered either as a matter of information or of subject material for teaching purposes.

The committee feels that in initiating such work, the expense incident to the establishment of a particular center or the erection of a special building should be avoided, but that if sufficient funds can be made available someone should be selected as a manager for this activity, his principal duty being to ascertain those who have been most successful in doing the particular bit of work that needs to be done at the moment, securing this cooperation, allocating the work, correlating the results, and devising the best means of placing such results in the hands of teachers. He should also devise means for encouraging teachers to utilize this material, and inaugurate a follow-up system whereby it could be ascertained how widely the material is being used and whether the results seem to indicate that the right procedure is being followed.

The committee also feels that rather than risk the permanent employment of a small group of men for this work, it would be wiser, especially in the initial stages of such activity, funds being available, to arrange for the retaining of well known talent on a temporary basis, permitting them to conduct their part of the work in their present locations and providing funds for such necessary travel as might be involved in arranging the material assigned to them. For example, let us suppose that Professor A has demonstrated his ability as a teacher in colloid chemistry. If funds were available, the manager would approach Professor A to bring together in a form believed suitable for the teacher all of the material in some field of colloid chemistry and would arrange with his college or university for the services of Professor A taking over all or such part of the salary obligations as circumstances might dictate. At the close of the work Professor A would take up his full teaching or other duties at his accustomed post. In this fashion the services of a large number of well qualified men could be obtained without running the risk of choosing the wrong men in the beginning, and in time certain men would prove so adept in work of the kind that wisdom might indicate their employment on a full-time basis for the Bureau. A valuable by-product would be the creation of a number of widely scattered centers of interest in this work.

The method of publishing and placing this specially prepared material in the hands of the teachers would have to depend upon circumstances. Conceivably existing mediums of publication like the *Journal of Chemical Education* would present one of the best methods for disseminating this material. Reprints, pamphlets, and monographs offer other methods.

Unquestionably teachers profit greatly from a multiplication of contacts and the less experienced teachers can be greatly helped by demonstrations of method. We therefore suggest for further consideration a proposal whereby certain teachers who have made a brilliant success at their work can be brought in contact with larger groups of teachers. It might be feasible to hold at irregular intervals state or regional meetings of chemistry teachers at which lectures and demonstrations involving the method of teaching would be given over a week-end period. On such occasions educators should be provided to discourse on methods of teaching, teachers could give demonstration lectures, with experiments, with motion pictures, and with other aids to teaching, and a helpful part of such a program would be an open forum on some selected topic. While the appearance of such teachers before actual classes might be very helpful, these appearances should take the form of special lectures to the class rather than a demonstration of methods of teaching, for if the latter were done the regular teacher might be caused some embarrassment and conceivably suffer from comparisons that would be made by the pupils between the special and the regular class sessions. However details of any demonstration must obviously be left for future consideration.

To encourage and indeed to insure attendance upon such meetings of teachers, funds might be wisely expended in meeting, say, one-half the actual travel expense of teachers who under such circumstances could probably obtain a part or all of the remainder from their school boards or others in authority. Should this prove too great a burden, it is possible that such expenditure could be limited to those especially invited, not because they can contribute much but because they really need experience, or it might be limited to those below a certain predetermined salary level.

Such meetings would not only insure better contact between teachers of the area but would bring them in contact with these specialists, who in turn could advise the director of the Bureau of conditions found, of the reaction to the work being done, of new problems requiring consideration, etc. Obviously the Bureau would arrange such meetings, tours of the teachers selected, and other details.

As for research in the methods of teaching, it would seem possible that this could be given some attention without involving the Society in research in the field of pedagogy. The various schools of education are at work in this field and it might be useful to summarize and correlate their findings and advice, but since it seems evident that the best research in methods of teaching chemistry is actually going on in the class rooms of all successful, inspiring, and keen teachers, the first steps that might be taken under this Bureau for the extension of Chemical Education would be to secure and publish descriptions of the methods employed in those schools where the results with students indicate the success of the method.

It would seem highly desirable, indeed necessary, for the Committee on Chemical Education to seek the advice of the most successful teachers of chemistry as to the present needs in teaching, considering the problem from the viewpoint of secondary schools and of institutions of higher learning. In a matter of such import it is very needful to have the advice of competent persons not interested in the exploitation of any particular idea.

The committee offers the above suggestions to the council for reference to the Committee on Chemical Education, in the belief that a plan somewhat as outlined would avoid many of the errors that might be made in initiating a more ambitious project requiring far greater funds. It would postpone for some time decision as to whether or not the Bureau as a whole need to have a definite location, and such a plan would provide both the means and the time for the selection of such small staff as might ultimately prove desirable to carry on such work as the Bureau might ultimately perform with the greatest success for the extension of chemical education.

Names of members deceased since the last meeting, as printed in Proceedings, were presented to the Council and the Council stood a moment in respectful silence.

The following was then read to the Council and will be acted upon in due course, as required by the Constitution:

PROPOSED AMENDMENTS TO THE CONSTITUTION OF THE AMERICAN CHEMICAL SOCIETY

Purpose. To provide for the office of President-elect who shall serve for one year as an ex-officio member of the council, the Executive Committee and the Board of Directors. This plan would enable the President-elect to become thoroughly familiar with society matters and give him an opportunity to arrange his personal affairs before serving his one-year term as President. The arrangement automatically provides only one term for a President, and yet removes the objection previously urged against bringing in each year a new man, unfamiliar with the affairs of the Society. The plan also provides a more logical person to serve in place of the President in case of his disability, instead of allowing the office to pass to that one of the many Vice-Presidents who may happen to have been a member of the Society for the longest time.

ARTICLE IV

Officers and Manners of Election

Section 1. Insert "a President-elect" after the word "President," and change "nine directors" to "ten directors."

Section 2. Change "President" to "President-elect."

Section 3. Insert "the President-elect" after the word "President."

Section 4. Change "President" to "President-elect" in paragraphs 1, 3 (twice), 4 and 11.

Change the first clause of paragraph 13 to read:

"The terms of the officers so elected shall be as follows: For the President-elect, one year beginning with the first day of January following, after which he shall automatically become President for one year, or until his successor shall have been duly chosen."

Also add paragraph 14 as follows:

"If the President-elect for any reason be unable to serve, or to assume the Presidency, his place shall be filled by letter ballot of the council from among the other three who received the greatest number of nominating ballots for President-elect in the previous election."

Section 6. Change to read: "In case of absence, death, or inability of the President to perform the duties of his office, his position shall, during his disability, be filled by the President-elect."

ARTICLE V

Section 2. Add "the President-elect" after "the President."

AMENDMENTS TO THE BY-LAWS

By-Law 3, in the first paragraph of the amendment constituting the executive committee, insert "President-elect" after "President."

At the first election subsequent to the adoption of the amendments providing for a President-elect, the person receiving the largest number of votes of the Council shall become President, and the person receiving the second largest number shall become President-elect.

The Council then voted its thanks to W. P. Putnam, Chairman of the Executive Committee; to L. W. Rowe, Chairman of the Local Section, together with all other committee chairmen, assistants, and members of the Detroit Section responsible for executing the vast amount of detail work incident to so large a meeting; also to the considerable number of industrial and social organizations in Detroit and elsewhere who were patrons of the Detroit convention and who otherwise assisted in making the meeting possible.

The Council then adjourned.

CHARLES L. PARSONS, *Secretary*

President Rosengarten has appointed Prof. Marston T. Bogert, of Columbia Uni-

versity, New York City, as a delegate to represent the American Chemical Society at the "Seventh Congres de Chimie Industrielle," to be held at Paris, France, October 16 to 22, 1927. Also, Professor Bogert has been appointed a delegate to represent the Society at the "Centenaire de Marcelin Berthelot," to be held at Paris, France, October 23 to 26, 1927.

MEMBERS ELECTED BETWEEN JULY 15, AND SEPTEMBER 15, 1927

AKRON SECTION

McKinney, D. D.

CALIFORNIA SECTION

Mittelman, L.

CHICAGO SECTION

Kratz, E. M.

Thacker, Gilbert D.

CLEVELAND SECTION

Kline, Harry

COLORADO SECTION

Wakeham, Glen

CORNELL SECTION

Browne, Arthur Westgate

DETROIT SECTION

Chase, George F.

Cocanower, Lloyd E.

Jacobson, Mark

Larrowe, James F.

Sutton, Carroll R.

FORT WAYNE SECTION

Moore, Raymond F.

GEORGIA SECTION

Ford, T. Bartow, Jr.

KANSAS CITY SECTION

Hollman, E. G.

Martin, H. Arthur

LOUISIANA SECTION

The Celotex Co.

NEW YORK SECTION

Duisberg, Walter

Fetherston, Franklin R.

Gray, Alvin N.

Isles, Frederick Wilson

Wenman, Frederick A.

Winchell, Clarence Wm.

NORTHEASTERN SECTION

Klein, Louis

Lobdell, Alban J., Jr.

McKinnon, Allen G.

NORTH JERSEY SECTION

Segessemann, Ernest G.

OKLAHOMA SECTION

Althausen, Darrell

Doennecke, Henry W.

PITTSBURGH SECTION

Dimit, Beatty H.

PUGET SOUND SECTION

Yakima Valley Spray Company

RHODE ISLAND SECTION

Butterworth, Walton B.

ROCHESTER SECTION

Titus, Robert N.

SOUTHEASTERN TEXAS SECTION

Smith, Homer A.

UNIVERSITY OF ILLINOIS SECTION

Drake, Edwin H.

Shirkcliff, Robert S.

Symons, G. E.

VIRGINIA SECTION

Aspegren, Herman

WISCONSIN SECTION

Lenher, Sam

NO SECTION

Clark, Roland Vivian

Csanyi, Ladis H.

Heard, R. D. H.

Johnson, Paul H.

Simms, Alderson

Smithells, Arthur

Von Wilm, Alexander

The Wilbur-White Chemical Co

DECEASED

BAYLES, F. T., 710 N. Bellview, Indianapolis, Ind. Died, 1927.

BOLTWOOD, BERTRAM B., Box 1813, Yale Station, New Haven, Conn. Died, August 14, 1927.

HILL, HERBERT M., 20 W. Eagle St., Buffalo, N. Y. Died, July 3, 1927.

HOLT, NORMAN R., c/o du Pont Co., 54 New Broad St., London, E. C. 2, England. Died, 1927.

TALBOT, HENRY P., Mass. Inst. of Tech., Cambridge, Mass. Died, July 18, 1927.

WEYMAN, GEOFFREY, Dene House Ellison Place, Newcastle-on-Tyne, England. Died, 1927.

Proceedings

COUNCIL MINUTES

At the Los Angeles meeting of the American Chemical Society in August, 1925, the Division of Industrial and Engineering Chemistry appointed a committee to look into the situation of automobile exhaust in relation to the hazards of carbon monoxide escaping therefrom and the waste of gasoline incident to allowing automobile engines to run while standing.

The Committee reported as follows:

"There are over 2,000,000 trucks and taxicabs in the United States whose drivers keep engines running while parking. This practice results in a loss of more than \$80,000,000 per annum and the escape of carbon monoxide in excess of 250,000,000,000 cubic feet. Aside from the monetary loss, we already have more than a comfortable amount of carbon monoxide in congested thoroughfares from 15,000,000 or more passenger cars. Exhaust gases average over 7% CO.

"At the Los Angeles meeting in 1925, your division appointed a committee whose report has been delayed because of the illness of the Chairman. This Committee now makes the following recommendations:

"1. That your division ask the President of the American Chemical Society to appoint a representative who, with similar representation from the National Safety Council, the American Automobile Association, the American Medical Association, the United States Chamber of Commerce, and such other organizations as the President may select, shall constitute a committee with duties that shall include:

"(a) The encouragement of use of automatic starting devices for trucks and taxicabs as cranking is dangerous and feared by many drivers.

"(b) The encouragement of researches towards the lowering and possible elimination of carbon monoxide in exhaust gases.

"(c) The giving of adequate publicity regarding the dangers of carbon monoxide poisoning, and the necessity of fuel economy, through the public press and various other channels.

(Signed) Alexander Silverman, *Chairman*,
Erle M. Billings
A. C. Fieldner"

The Division of Industrial and Engineering Chemistry at the Detroit meeting in September, 1927, approved the report and President Rosengarten has appointed Professor Alexander Silverman of the University of Pittsburgh the representative of the American Chemical Society on the joint committee which is being appointed to study the situation.

CHARLES L. PARSONS, *Secretary*

President Rosengarten has appointed Prof. E. W. Rockwood, of the University of Iowa, Iowa City, Iowa, the Society's representative at the inauguration of Dr. Herbert John Burgstahler as President of Cornell College, Mount Vernon, Iowa, on November 18, 1927.

LIST OF MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND NOVEMBER 15, 1927

AKRON SECTION

Duffy, C. C.
Jones, Paul Carlton
Kern, Ervin S.

ALABAMA SECTION

Jackson, J. T.

CALIFORNIA SECTION

Larsen, Louis G.
Lyon, Alice L.
MacMartin, J. Norbert
McKenna, Philip M.
Miller, Sally
Thompson, John H.

CHICAGO SECTION

Anderson, Ralph S.
Boholm, Ernest G.
Gans, David Manus
Guiohas, Christo J.
Hayson, Frank M.
Hoen, R. E.
Liebl, Florence I.
Lossy, Alex. S.
Mayser, Richard D.
Parkhurst, George L.
Schwartz, Stephen
Washburn, R. M.
Wilson, Ray S.

CINCINNATI SECTION

Lurie, Jacob

CLEVELAND SECTION

Richards, Leo D.
Sandel, Clayton

COLORADO SECTION

Oberg, Aaron G.
Robinovitch, Louise G.

CORNELL SECTION

Phelan, Earl Walter
Ritson, Daniel D.

DETROIT SECTION

Parker, Robert Ross
Pratt, Arnold E.

FLORIDA SECTION

West, Frances L.

GEORGIA SECTION

LeConte, Joseph N.
Myrick, Lillas

INDIANA SECTION

Ball, William H.
Gasper, George
Harrington, Paul J.
Peyton, Floyd A.

IOWA SECTION

Snyder, Robert G.
Thomas, Bert E.

KANSAS CITY SECTION

Naudet, P. T.

LEHIGH VALLEY SECTION

Brown, Richard A.
Jones, H. C.
Zimmermann, Erich Karl

LEXINGTON SECTION

Watson, Russell Frank

LOUISIANA SECTION

Danneker, John Martin
Gilfoil, W. S.
Heard, Joseph R.

MAINE SECTION

Sweetman, Marion Deyoe

MARYLAND SECTION

Curry, James R.
Druhan, John J.
Findley, F. G.
Pickett, Lucy Weston
Wallace, Dorothy E.
Young, Hugh H.

MIDLAND SECTION

Mong, Lewis E.

MILWAUKEE SECTION

Cramer, Robert

MINNESOTA SECTION

Blosjo, Herbert H.
Dombrowski, John F.
Gehrenbeck, Gilbert B.
Jallings, Kenneth R.
Murray, Robert C.

NASHVILLE SECTION

Houston, Edward C.

NEW HAVEN SECTION

Fleischer, Joseph

NEW YORK SECTION

Alter, Abraham
Denzler, Harry Louis
Dotti, Louis B.
Johnson, Eric Philip
Kellogg, Minerva
Kobbe, Wm. H.
Majewski, Frank M.
McGowan, Ellen B.
Smith, Richard A.

NORTH CAROLINA SECTION

Clifford, Alfred T.
Southern, J. A.

NORTH JERSEY SECTION

Flaherty, Edmund M.
Greene, Mildred C.
Hendry, Richard M.
Hunter, Elizabeth
Mertens, Fred T.
Thatcher, Frederick M.
Warner, C. W.
Weisberger, Hugo E.

NORTHEASTERN SECTION

Barton, Bernard
Birge, Margaret
Bockstrom, Carl W.
Buck, Lucien
Clark, Benjamin F., Jr.
Foley, Arthur
Gustaferr, Joseph A.
Hamilton, Charles H.
Hess, Lewis
Lehman, E. J.
Linehan, Joseph D.
Owen, Randolph J.
Poland, George L.
Rand, Katharine
Whittemore, Russell G.

NORTH WESTERN UTAH SECTION

Wernimont, Grant

OKLAHOMA SECTION

Cary, Earl E.
Gates, Ralph E.

PHILADELPHIA SECTION

Cranmer, Walter W.
Powell, Garfield
Robinson, Robert
Simon, Walter O.
Singleton, Wm. F.

PITTSBURGH SECTION

Cruikshank, Charles C.
Sipple, Horace L.

PORTO RICO SECTION

Margarida, Fernando

PURDUE SECTION

Block, Harry W.
Breden, C. R.
Enfield, George H.
Muir, Dwight C.
Yund, C. C.

ROCHESTER SECTION

Berger, Kenneth H.
Englert, Justin F.
Spengler, John Arthur

ST. LOUIS SECTION

Elder, Thomas G.

SOUTHERN CALIFORNIA SECTION

Anker-Holth, S. C.
Cox, Lloyd B.
Donaldson, Wm. E.
Hoag, Chauncey Allen
Holton, Homer H.
Johnston, Genevieve E. M.
Whistler, Arthur McLeod
Wright, William R.

SYRACUSE SECTION

Birtley, Theodore D.
Ernst, Frank A.
Snyder, J. P.

TOLEDO SECTION

Lux, Marian E.

UNIVERSITY OF ILLINOIS SECTION

Cortelyou, W. P.
Harvey, Mary Gertrude
Manley, Ralph H.
Yohe, G. Robert

UNIVERSITY OF MICHIGAN SECTION

Drummond, David H.
Ho, Kai

VIRGINIA SECTION

Carmony, Harold E.
Garrels, John C.

WASHINGTON SECTION

Hazell, Joseph W.
Schober, Edward M., Jr.

WESTERN NEW YORK SECTION

Munro, Albert E.
Stevens, W. H.

WISCONSIN SECTION

Roeseler, Oscar E.

NO SECTION

Albin, T. C.
Billings, A. W. K.
Bruza, Boris
Buchan, John E.
Canadian Celanese Limited
Chemical Department of Cairo
Drummond, Jack Cecil
Excel Company, Ltd.
Finlayson, Guy
Frye, A. L.
Gaus, Frank L.
Hastilow, C. A. F.
Hauff, Thor. W.
Hubbard, Carroll C.
Kellogg, George W.
Lee, H. Atherton
Maxwell, Robert W.
McGowan & Sons, Inc., P. J.
McNulty, Catherine E.
O'Shaughnessy, F. R.

Park, Bart
 Peacock, William
 Pius, Sister M.
 Power, Charles D.
 Schmitt, Philip

Sierp, Friedrich
 Sypesteyn, J. C. Kaars
 Wallace, Joe W.
 Waymouth, John F.
 Wischer, Paul

DECEASED

Ball, Samuel Francis, 289 East 201st St., New York City.
 Beale, Horace A., Jr., Parkesburg Iron Co., Parkesburg, Pa. Died, Sept. 6, 1927.
 Burr, E. C., 1722 Vallejo St., San Francisco, Cal. Died, Sept. 2, 1927.
 Camp, J. M., Carnegie Bldg., Pittsburgh, Pa. Died, Oct. 24, 1927.
 Fennel, Charles T. P., 614 Court St., Cincinnati, Ohio.
 Fowler, Edward J., 18th and Harrison Sts., San Francisco, Cal. Died, Oct. 19, 1927.
 Hallock, Albert P., 19 Radford Place, Yonkers, N. Y. Died, June 12, 1927.
 Hunziker, Aug., Weidman Silk Dyeing Co., Paterson, N. J. Died, April, 1927.
 Kennedy, Frederic G., 2114 W. Columbia Ave., Philadelphia, Pa. Died, Aug. 30, 1927.
 Orndorff, W. R., Cornell University, Ithaca, N. Y. Died, Nov. 1, 1927.
 Rust, Roger Allen, 105 Washington St., Gloucester, Mass. Died, May 4, 1927.
 Silver, C. Albert, 905 W. Johnson St., Madison, Wis.
 Snyder, Harry, 1800 Summit Ave., Minneapolis, Minn. Died, Oct. 12, 1927.
 Wagner, Leonard R., 1209 Olivia St., Ann Arbor, Mich. Died, Feb. 21, 1926.
